

Invited Review

The inventory of interstellar materials available for the formation of the solar system

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Abstract—Tremendous progress has been made in the field of interstellar dust in recent years through the use of telescopic observations, theoretical studies, laboratory studies of analogs, and the study of actual interstellar samples found in meteorites. It is increasingly clear that the interstellar medium (ISM) contains an enormous diversity of materials created by a wide range of chemical and physical processes. This understanding is a far cry from the picture of interstellar materials held as recently as two decades ago, a picture which incorporated only a few generic types of grains and few molecules.

In this paper, I attempt to review some of our current knowledge of the more abundant materials thought to exist in the ISM. The review concentrates on matter in interstellar dense molecular clouds since it is the materials in these environments from which new stars and planetary systems are formed. However, some discussion is reserved for materials in circumstellar environments and in the diffuse ISM. The paper also focuses largely on solid materials as opposed to gases since solids contain a major fraction of the heavier elements in clouds and because solids are most likely to survive incorporation into new planetary systems in identifiable form. The paper concludes with a discussion of some of the implications resulting from the recent growth of our knowledge about interstellar materials and also considers a number of areas in which future work might be expected to yield important results.

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INTRODUCTION

Dense interstellar molecular clouds are the birth sites of new stars and planetary systems (*cf.*, Pudritz and Fich, 1988; Podosek and Cassen, 1994). The actual formation process is not completely understood, but it is clear that new stars are made from the gas and dust that make up the parent interstellar cloud. Thus, the identification of materials present in dense molecular clouds, especially in the vicinity of newly formed stars, should provide information about the materials present when our solar system formed. In other words, a compositional "inventory" of interstellar dense molecular

clouds represents a constraint on stellar formation models and helps place the interstellar grains found in meteorites within a broader astrophysical context.

It has been known for some time that the interstellar medium (ISM) contains gas and dust. This was initially demonstrated by Trumpler (1930) who noted that different measurement techniques gave different distance estimates to star clusters within our galaxy and that the disparate values could only be explained by the presence of a general "absorption" produced by the interstellar medium itself. However, for the next 30 years there was very little advancement in our understanding of the nature of the materials responsible for the absorption. While the first three molecules (CH, CH⁺, and CN) were detected by optical spectroscopy around 1940, one of the biggest steps towards demonstrating that a substantial fraction of interstellar material was not simply atomic gas came with the later advent of radio telescope technology. Using radio spectral techniques, Weinreb *et al.* (1963) made the first detection of the rotation lines of a molecule in the interstellar medium, namely the hydroxyl radical (OH). While the presence of this molecule had been predicted as early as 1953 (Shklovsky, 1953), many felt that it was unlikely that molecules could survive in any abundance in the harsh radiation environment thought to exist in the ISM. Since 1963, the number of gas phase molecules identified in space has grown at an ever increasing rate. My college astronomy text (Smith and Jacobs, 1973) lists 20 molecules (not counting isotopic variants), the most complex having seven atoms. By 1980, the list had grown to 52 and included molecules as large as 11 atoms (Mann and Williams, 1980). Current lists contain closer to 100 molecules and at least one molecule containing 13 atoms has been detected (van Dishoeck *et al.*, 1993).

While radio astronomy has amply demonstrated that the interstellar medium contains molecules, it is only capable of identifying materials in the gas phase (see Techniques). Until the advent of infrared astronomy, most of our knowledge about the solid fraction

of the absorbing material in the ISM was derived from (1) the overall shape of the extinction curve in the visible and ultraviolet, (2) the wavelength dependence of polarization produced by the dust, and (3) the gas-phase depletions of various elements determined from UV spectroscopy of stars (*cf.*, Greenberg and Hong, 1974; Mathis *et al.*, 1977; Jenkins, 1989; Martin, 1989). These provided some general constraints on the nature of the solids and suggested that the dust contained several different populations. Unfortunately, information gained in this way does not yield unique identifications of dust components, as evidenced by the large number of different models that have been published to account for the extinction curve. Fortunately, the advent of infrared astronomy, particularly infrared spectroscopy, has helped considerably (see Techniques). We now know that a large portion of the heavier elements in both the dense and diffuse ISM are in molecular form in solid grains and ices rather than in the gas phase, and the identity of a substantial fraction of this material has been determined (*e.g.*, Allamandola and Sandford, 1988; Sandford, 1996).

Of course, a discussion of the composition of everything in the interstellar medium would span a vast range of physical and chemical environments and involve a number of scientific disciplines. I will place a number of restrictions on the extent of this review in order to (1) keep within the areas in which I feel I have some expertise and (2) be able to count the number of citations without having to resort to exponents. I will largely restrict myself to materials in interstellar dense molecular clouds since they are where stars form. I will also concentrate largely on solids because they contain a major fraction of the heavier elements in clouds and because these materials are most likely to survive incorporation into new planetary systems in identifiable form. However, dense clouds are not well-defined, long-lived entities. Instead, they are dynamic objects that are formed from materials in the diffuse ISM and destroyed on time scales of 10^6 – 10^8 years (Elmegreen, 1987). In addition, the clouds undergo significant physical and chemical evolution on even shorter time scales (Prasad *et al.*, 1987; Scalo, 1987). Ultimately, the very same stars that are made in the cloud are responsible for its dispersal *via* radiation pressure, supernovae explosions, *etc.* The efficiency of star formation, as measured by the fraction of the material in the original cloud that ends up in new stellar systems, is quite low. Molecular clouds can contain 10^5 – 10^6 solar masses, while the combined mass of the stars in a typical open cluster is usually $<10^3$ solar masses, suggesting efficiencies of $<1\%$. As a result, it is thought that materials in space are constantly being mixed between the dense ISM and the more diffuse intercloud ISM, and some discussion of the materials found in the diffuse ISM is also merited. Similarly, materials formed in circumstellar environments, for example in the atmospheres of late type stars, will also be mixed into the diffuse and dense interstellar media, and some discussion about these materials is also included.

Finally, I will not spend much time on the interstellar materials found in meteorites and interplanetary dust particles (IDPs) since this work is likely to be familiar to most readers of *Meteoritics & Planetary Science* and since this field is presently well supplied with current papers and excellent reviews (see, for example, Anders and Zinner, 1993; Ott, 1993; Huss *et al.*, 1994; Huss and Lewis, 1995). These samples represent only a portion of the interstellar inventory, namely the fraction of material that is capable of surviving exposure to the interstellar medium, passage through the protosolar nebula, incorporation into a meteoritic parent body (along with all its subsequent evolution), and ultimately, the abuse

of the chemical dissolution process used to wrest the grains from the meteorites. Thus, the population of collected interstellar dust is the result of a number of selection effects and the telescopic observations provide a means of placing these grains within the context of the entire interstellar inventory of materials. Despite the selection effects, the meteoritic grains provide unique information that can never be supplied by purely remote observations, and they have the singular advantage of being samples of real interstellar dust. Thus, they provide a critical "ground truth" against which models can be compared and they should prove to be a constant source of irritation to theorists in astronomy (always a good thing!). Given the substantial extant literature mentioned above, I will largely restrict discussions about the meteoritic samples to points where they assist in the interpretation of the astronomical data or vice versa.

TECHNIQUES

In principle, the entire population of interstellar dust, in all the varied environments in which it is seen, can be studied telescopically. However, the interpretation of remote sensing data is complicated by the fact that the actual materials are not available for study in the laboratory and therefore can only be characterized in a limited manner. This problem is partially alleviated by using laboratory studies of analog materials to help interpret the telescopic observations, but information obtained from grains in space will never attain the degree of detail already "routinely" gathered from meteoritic samples. Nonetheless, the hope is that the strengths of these two complimentary fields can ultimately be combined to give a comprehensive view of the interstellar dust population.

Telescopic Observations and Spectroscopy

Any discussion of the material residing in the ISM must, of necessity, rely heavily on results obtained using the techniques of radio, submillimeter, and infrared spectroscopy. This is in part because much of the material lies in or behind large column densities of dust and gas that completely block the passage of visible photons. Photons at infrared and longer wavelengths can be used to probe these materials because they can penetrate larger column densities. Radio and submillimeter observations are best suited for identifying gas-phase species. In principle, the identification of both gas- and solid-phase materials is possible at infrared frequencies, but the limited spectral resolution of most astronomical spectrometers has largely limited their use to the study of solids. However, the advent of higher resolution telescopic infrared spectrometers is now allowing the study of gas-phase species as well (*cf.*, Evans *et al.*, 1991). Both wavelength regions are discussed below, but I will concentrate on the infrared since the focus of this review is on interstellar solids.

Radio and Submillimeter Astronomy—The energies associated with the purely rotational transitions of gas-phase molecules fall in the submillimeter and radio portion of the electromagnetic spectrum. As a result, all molecular species with allowed rotational transitions involving a rotating dipole moment produce narrow, characteristic bands at these frequencies. Armed with rest frequencies determined in the laboratory, it is therefore possible to search for gas-phase species in the ISM by looking for their characteristic bands (*cf.*, Turner, 1991). This gives radio studies the substantial advantage that molecular identifications are very secure, especially if multiple transitions of the same molecule are observed.

It is also possible to determine the temperature of the gas by studying the strengths of bands from different transitions of the

same molecule and noting whether the bands are in absorption or emission. In addition, since these rotation lines are intrinsically narrow, it is often possible to use the band positions and profiles to determine the absolute and dispersion velocities of the gas. Armed with this information, many of the characteristics of the environment can be derived (temperature, pressure, dynamics, *etc.*) (*cf.*, Myers, 1983; Myers and Benson, 1983; Mundy *et al.*, 1990; Blake *et al.*, 1992). Thus, it is not surprising that radio spectral techniques have proven to be a major workhorse for astronomers interested in interstellar molecules and dense molecular clouds.

Radio observations do have several disadvantages, however (as do all techniques). One disadvantage is that abundance determinations are model dependent. Also, only gas-phase species whose transitions involve rotating permanent dipole moment can be studied. As we shall see, the majority of interstellar materials in dense molecular clouds fail to meet these criteria.

Infrared Astronomy—As in the radio technique, spectroscopy at infrared frequencies allows one to identify the composition of materials by the detection of molecular transitions. The infrared spectral region falling between 2 and 30 μm (5000 to 330 cm^{-1}) spans the energy range associated with the fundamental interatomic vibrations of virtually all the molecular bonds associated with the cosmogenically most abundant species (Bellamy, 1960; Silverstein and Bassler, 1967). Figure 1 contains a schematic diagram summarizing the frequency regions in which many of the more common vibrations fall. The infrared spectrum of a molecule consists of the superposition of many different bands, each associated with specific molecular bonds or chemical functional groups. Since much of the discussion that follows relies heavily on infrared spectroscopy and since many readers may not be conversant with this discipline, a brief description of the technique is given below.

Figure 2 displays the infrared spectra of several laboratory samples that illustrate some of the strengths and weaknesses of using infrared spectroscopy to identify materials. The traces in Fig. 2a

and b show the infrared spectra of $\text{H}_2\text{O}:\text{CO}_2 = 20:1$ gas- and solid-phase samples, respectively. Several differences are immediately apparent. In the gas phase, both the H_2O and the CO_2 are free to rotate, and each of the main rotational-vibrational band systems show detailed structure resulting from the superposition of rotational transitions on the vibrational fundamental. In contrast, rotation is not possible when these molecules are in the solid phase and the multiband rotation structure collapses into simple, broader bands. These bands are broader than the individual rotation lines because of site effects in the solid. Different molecules in the ice experience different perturbations by their neighbors and the result is a distribution of vibrational frequencies centered near the fundamental frequency of the vibrational mode (see Allamandola, 1984). The differences in band position and profile due to interactions with neighboring molecules are referred to as matrix effects (see Hagen *et al.*, 1983 and Sandford *et al.*, 1988 for examples).

The intrinsic absorption strength of a mode is a function of quantum mechanical selection rules and the dipole change associated with the vibration (*cf.*, Bellamy, 1960; Silverstein and Bassler, 1967). For example, the asymmetric $\text{O}=\text{C}=\text{O}$ stretch of CO_2 near 2340 cm^{-1} is very strong because it involves a large change in dipole moment, while the symmetric $\text{O}=\text{C}=\text{O}$ stretch near 1385 cm^{-1} is undetectable because it involves no change in dipole moment (see Fig. 2a,b; Sandford and Allamandola, 1990). In most cases, the strength of a given absorption is the same within factors of 2 to 3 for the gas and solid phases, but there are important exceptions. Molecules that form strong intermolecular bonds can be significantly perturbed by their neighbors in the solid state, and this can alter the intrinsic strength of the bands. The best example of this is the 3250 cm^{-1} O-H stretching vibration of H_2O . In the solid phase, this band's intrinsic strength increases by a factor of ~ 100 relative to

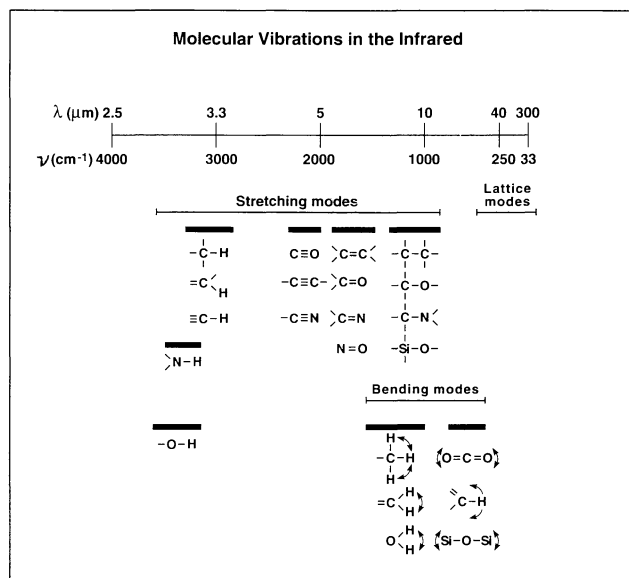


FIG. 1. A schematic drawing of the infrared spectral region between 4000 and 300 cm^{-1} (2.5–33 μm). The range over which the interatomic vibrations of a variety of common molecular bonds fall are signified by the horizontal bars. This portion of the infrared spans virtually all the fundamental vibrational modes of the different chemical bonds associated with the most common elements. (Figure adapted from Allamandola, 1984.)

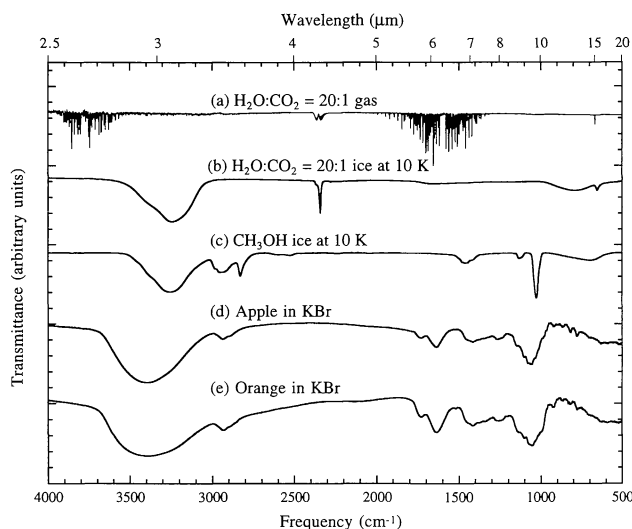


FIG. 2. The 4000–500 cm^{-1} (2.5–20 μm) infrared spectra of (a) a gas phase $\text{H}_2\text{O}:\text{CO}_2 = 20:1$ sample at room temperature, (b) a solid $\text{H}_2\text{O}:\text{CO}_2 = 20:1$ ice sample at 10 K, (c) a solid CH_3OH (methanol) ice sample at 10 K, (d) a Granny Smith apple at room temperature, and (e) a Sunkist navel orange at room temperature. The apple and orange samples were prepared using standard salt pellet techniques (Sandford, 1995). These spectra demonstrate the ability of infrared spectroscopy to distinguish between solid- and gas-phase species and to assist with the identification of molecular species. The last two spectra, however, demonstrate that infrared spectroscopy can have great difficulty in detecting the specific molecular differences between different complex systems that contain molecules with similar chemical functional groups.

the gas phase due to the strong H-bonding that occurs between neighboring molecules (Allamandola, 1984). There can also be significant differences between the gas and solid phases for vibrational modes that are classically forbidden in the gas phase. For example, the stretching modes of gas phase N_2 and O_2 do not normally produce infrared absorption bands because they do not involve a change in dipole moment. However in the solid state, the perturbations of these molecules by their neighbors can make these modes weakly infrared active (*cf.*, Ehrenfreund *et al.*, 1992; Bohn *et al.*, 1994). Thus, one of the advantages of infrared spectroscopy is that it can provide a good means of determining the balance between gas- and solid-phase components of the same molecules and provides information about the matrix conditions within the solids.

Comparison of Fig. 2b and c demonstrates another advantage of infrared spectroscopy. Since it is the nature of the chemical bonds that defines the strengths and frequencies of infrared bands, individual compounds will produce characteristic spectra that reflect the chemical bonds they contain (*i.e.*, every molecule has an infrared "fingerprint"). For example, in Fig. 2b and c it is easy to see how H_2O and CH_3OH (methanol) can be identified and distinguished from each other using only their infrared spectra.

Ironically, the dependence of the spectrum on molecular bonding is also one of the technique's weaknesses. Molecules having a different combination of molecular bonds will produce different spectra, but individual spectral features may be nearly identical if similar molecular functional groups are responsible. For example, while the spectra of H_2O and CH_3OH shown in Fig. 2b and c are clearly very different, both have a nearly identical absorption band near 3250 cm^{-1} because both contain an $-OH$ group that undergoes stretching vibrations in a similar polar environment. Thus, molecular identifications based on only one or even two observed spectral features are often uncertain. Since it is rarely possible to obtain astronomical infrared spectra that cover the entire infrared, this can be a serious issue for the remote identification of materials in space. Even with complete spectral coverage, clear cut identifications are not always guaranteed, especially if complex molecular systems containing similar mixtures of similar bonds are involved. The infrared spectra of apples and oranges provide a good example of this problem (Fig. 2d,e). (Who says you can't compare apples and oranges!) Another excellent example is provided by the infrared spectra of DNA. Strands of DNA can differ from each other in literally millions of ways and yet their infrared spectra will be virtually identical because they all consist of the same four chemical moieties. (For example, the infrared spectra of our DNA and that of Brewer's Yeast are identical. A humbling thought!)

Thus, the use of infrared spectroscopy has the advantages that it allows the astronomer to probe large column densities of material, identify chemical functional groups present, and understand their physical state. The technique's chief disadvantages are that it is insensitive to molecular vibrations that produce no change in dipole moment, and the identification of individual molecular species can be difficult if there is confusion from overlapping bands in complex molecular systems.

Infrared spectral features can be produced both in absorption and in emission, depending on the materials and their environment.

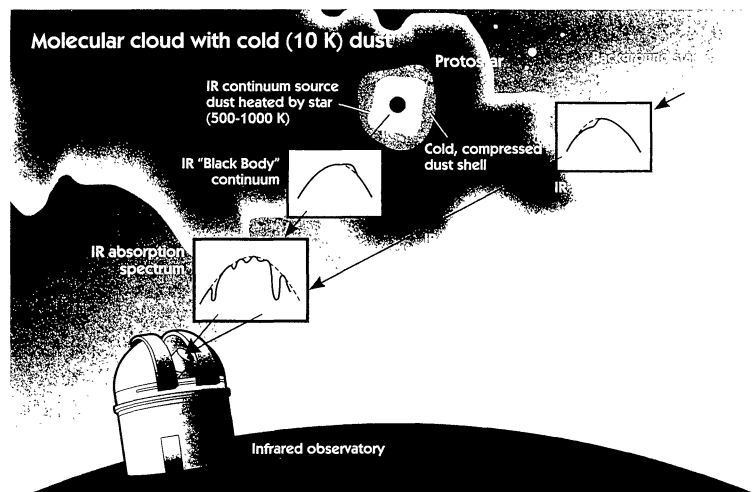


FIG. 3. A schematic drawing of how materials in dense molecular clouds produce absorption bands in the infrared spectra of embedded and background stars. The measured infrared radiation is often associated with an embedded protostar that is forming from the surrounding cloud material. In this case, the emission consists of radiation from both the embedded protostar itself and the surrounding dust that is heated by the protostar. In the case of background infrared sources, the original infrared radiation comes from a star (usually a cool, late-type star) that lies behind the cloud and which may be completely unrelated to the cloud itself. In either case, the original infrared energy spectrum is a quasi-blackbody distribution that may contain some spectral structure associated with the source and that suffers selective absorption as the radiation passes through dense cloud materials that lay along the line-of-sight between the source and the observer.

In dense molecular clouds, where temperatures are very low ($10\text{ K} < T < 60\text{ K}$), most features are seen in absorption. Figure 3 contains a schematic showing how dense cloud materials produce absorption bands in the infrared spectra of embedded or background stars. The source of the original infrared radiation is often a protostar that is forming from the surrounding cloud material. In this case, the original infrared "source" consists of a combination of emission from the embedded protostar itself and emission from nearby dust heated by the protostar. In the case of background sources, the original infrared radiation comes from a star that lies behind the cloud and that may be completely unrelated to it. In either case, the original infrared energy distribution is a quasi-blackbody spectrum that may or may not contain some features intrinsic to the source. This energy spectrum then suffers frequency-dependent extinction as it passes through the cloud, and it is this extinction that can be used to probe the composition of the cloud material. It should be kept in mind that the nature of such observations places limitations on the interpretations of the spectra. First, individual spectra represent the superposition of all the absorption along the line-of-sight. It is often difficult to determine whether all the components identified in a spectrum are homogeneously mixed within the cloud or whether they are separated into different, colinear environments. In addition, it is not always clear which spectral features are due to the cloud and which are intrinsic to the source (in the case of embedded protostars, there may even be features associated with the interaction of the two!). Despite these limitations, the interpretation of such spectra has provided major insights into the composition of the clouds from which stars form.

Laboratory Studies

The proper interpretation of telescopic infrared data requires the availability of the laboratory spectra of relevant materials obtained under appropriate conditions. This is true of both gas-phase and

solid-phase materials. Again, I will restrict my discussion largely to the solids, although much of what follows holds for gas-phase species as well.

In most cases, the comparison of laboratory and astrophysical spectra are needed to provide the original identification of the materials responsible for interstellar spectral features. Once a tentative assignment is made, the laboratory spectra can be used to identify other spectral features associated with the molecule in question. The interstellar spectra can then be searched for these additional features to test the original identification. Additional laboratory experiments can also be made to determine the astrophysical and astrochemical implications of the identification, predict the presence of other chemical species, infer environmental conditions, *etc.*

Quantitative laboratory studies can also assist with the determination of the abundances of materials in space. Assuming the sample is not optically thick, the column density, N (molecules cm^{-2}), of an absorbing material can be determined from:

$$N = \frac{\int \tau_i(\nu) d\nu}{A_i} \approx \frac{\tau_{i\max} \Delta\nu_{1/2i}}{A_i} \quad \text{Eq. (1)}$$

where $\tau_i(\nu)$ is the frequency-dependent optical depth (absorbance) of an absorption band, $\tau_{i\max}$ is the maximum optical depth of the band, $\Delta\nu_{1/2i}$ is the full-width-at-half-height (in cm^{-1}) of the band, and A_i is the band's integrated absorbance (in cm molecule^{-1}) as determined from laboratory studies (*cf.*, d'Hendecourt and Allamandola, 1986; Hudgins *et al.*, 1993). Similarly, the laboratory measurement of the real and imaginary parts of the index of refraction ($n = n + ik$) of relevant materials (*cf.*, Roush *et al.*, 1991; Hudgins *et al.*, 1993, 1994) are critical for modeling the spectral effects of grain size distributions, reflection, *etc.* (*cf.*, Pendleton *et al.*, 1990). For specific examples of the types of techniques used in the laboratory to assist with the interpretation of astronomical data, the reader is invited to see Allamandola and Sandford (1988), Moore and Tanabé (1990), and Bernstein *et al.* (1995).

INTERSTELLAR PROCESSES

The population of materials in the interstellar medium is very diverse. This diversity is due to the variety of sources that eject material into the ISM and the many evolutionary processes that operate on these materials after their formation. Some of the major evolutionary processes that are thought to control the interstellar dust population are briefly discussed below.

Sources and Ejection into the Interstellar Medium

After the Big Bang, the universe was thought to consist largely of H and He. Heavier elements were subsequently formed as the result of nucleosynthesis in stars and it is these heavier elements from which all other interstellar materials but H_2 are formed. Thus, virtually all the atoms found in interstellar materials other than some of the H and He are the result of stellar nucleosynthesis followed by ejection from the parent star. While many of these elements may escape their parent stars as single atoms, there is extensive observational (*cf.*, Gehr, 1989) and meteoritic (*cf.*, Anders and Zinner, 1993) evidence that some of the elements escape in the form of molecules and grains.

Only a brief overview of the wide variety of sources and their products is provided here. Some additional information on sources will be provided in subsequent sections where individual types of material are discussed. More comprehensive reviews of the sources of material ejected into the ISM can be found in Tielens and

Allamandola (1987), Bode (1988), Gehr (1989), Tielens (1991), and Dorschner and Henning (1995).

In general, the main sources of material ejected into the ISM are stars nearing, or at, the end of their main sequence lifetimes (*i.e.*, stars which have exhausted the H in their cores). Conversion to other subsequent, short-lived nucleosynthetic processes (He burning, *etc.*) results in the accelerated production of heavier elements but also severely compromises the stability of the star. Depending on the conditions within the star, this can result in the relatively "gentle" ejection of material in the form of strong winds (carbon stars, planetary nebulae, *etc.*) or explosive ejection (novae, supernovae) (*cf.*, Bode, 1982, 1988; Woosley and Phillips, 1988).

The nature of the materials ejected into the ISM is dependent on the history of nucleosynthesis in the stellar source and on the pressure-temperature conditions existing in the outflow (*cf.*, Gail and Sedlmayr, 1987). One of the major components of interstellar ejecta is the molecule CO, because of both its great stability and the high abundance of C and O in most ejecta. As a result, the general character of the ejecta is a function of C/O ratio in the source. Sources having $\text{C/O} > 1$ will produce CO with the excess C forming other C-rich phases such as graphite or amorphous carbon. Sources having $\text{C/O} < 1$ will produce CO with the excess O forming O-rich phases such as oxides or silicates.

Grain Destruction and Evolution

Once ejected into the interstellar medium, molecules and grains are subjected to a wide variety of destructive processes. For example, gas-phase molecules are destroyed by UV photolysis in the diffuse ISM and dust is destroyed by astration (*i.e.*, incorporation into newly forming stars). However, the main source of grain destruction is through the erosion, vaporization, and shattering of grains by the passage of interstellar shock waves. These shocks are not of the kind that meteoriticists are familiar with, namely those generated by the collisions of two solid bodies, but are instead supersonic disturbances driven by thermal pressure, radiative acceleration, or other mechanical sources. Such shocks result in the rapid and differential acceleration of gas and dust in the ISM. Sources of such disturbances include supernovae explosions, strong stellar winds, molecular outflows from premain-sequence stars, and cloud collisions. Smaller grains are destroyed largely by thermal sputtering in fast, nonradiative shocks while larger grains are destroyed by non-thermal sputtering and grain-grain collisions in radiative shocks (*cf.*, Seab, 1987; Shull and Draine, 1987; McKee, 1989; Jones *et al.*, 1994).

Our present understanding of these grain destruction processes is largely theoretical and leads to something of a dilemma with regard to time scales. Most studies that have modeled grain interactions with supernovae shock waves suggest grain destruction processes should be efficient and indicate time scales for grain destruction on the order of 5×10^8 years. Such time scales are substantially less than the injection times for new grains and suggest that most of the refractory material in interstellar grains must have accreted (or reaccreted) on the grains in the ISM (*cf.*, Seab, 1987; Jones *et al.*, 1994), although how this occurs is not at all clear. In any event, this suggests that most of the dust is heavily processed in the ISM and loses much or all of the heritage associated with its original formation site. However, comparisons of the destruction and injection time scales indicate that the fraction of grains injected by stars and as yet unmodified in the ISM could be on the order of 20% at any given time (*cf.*, McKee, 1989). Our limited knowledge of both destruction and injection time scales makes this value

somewhat uncertain, but it is compatible with the presence of at least some unaltered grains in the reservoir of material from which the early solar nebula formed.

Since most processes are more effective at destroying certain types of material than others, the ultimate population of interstellar material in a given environment is the result of a combination of many selection effects. Even ignoring the selection processes associated with the incorporation of interstellar grains in the proto-solar nebula, subsequent parent body evolution, and all the various chemical procedures used to obtain the grains from their parent meteorites, it is clear that the grains found in meteorites are already significantly biased towards "tougher" species. Thus, it should be kept in mind that the interstellar grains found in meteorites are most likely *not* representative of the general interstellar dust population. This is one area where telescopic observations and the study of meteorites can interact in a very useful manner; the interstellar grains found in meteorites can provide very detailed information on the properties of real, if somewhat atypical, interstellar materials, while the telescopic observations can place this information in proper context with regard to abundances, sources, *etc.*

Gas Phase Chemistry

Chemistry is expected to occur in the gas phase in dense molecular clouds, where densities are higher (typically 10^3 – 10^7 atoms cm^{-3}) and molecules can survive longer because they are screened from excessive UV radiation. Normal chemical reactions between neutral species will not proceed at any appreciable rate at the low temperatures characteristic of dense clouds because insufficient energy is available to overcome activation barriers. However, when one of the species is ionized, perhaps by an interaction with a cosmic ray or UV photon, this barrier is removed. Thus, most of the gas-phase chemistry occurring in dense clouds is expected to be the result of ion-molecule reactions. The reaction chains that might be expected to occur under typical interstellar conditions have been extensively examined over the years (*cf.*, Herbst, 1987, and references therein). Such models have had differing degrees of success in explaining the observed abundances of some gas-phase molecules. However, models that consider only gas-phase processes have difficulties explaining the abundances of many types of species, for example, alcohols (Charnley *et al.*, 1995). As discussed in the next section, this difficulty is largely due to the models' failure to account for the presence of grains.

One of the more interesting consequences of the ion-molecule reaction process (at least for meteoriticists) is that the products of such reactions should be enriched in D because mass fractionation effects are expected to be significant at such low temperatures (*cf.*, Dalgarno and Lepp, 1984). Evidence for this process is found in the large D-enrichments determined from radio observations of DCN/HCN (Jefferts *et al.*, 1973), $\text{DCO}^+/\text{HCO}^+$ (Hollis *et al.*, 1976), $\text{CH}_3\text{OD}/\text{CH}_3\text{OH}$ (Mauersberger *et al.*, 1988), *etc.* Since such enrichments most likely could not have happened in the early solar nebula (Geiss and Reeves, 1981), the detection of D-enrichments in meteorites has long been considered to be evidence for the survival of interstellar products into the solar system (see Zinner, 1988). As we shall see later, ion-molecule chemistry is only one of several different ways in which interstellar species can become D-enriched.

Condensation and Gas-Grain Chemistry

New stars are born in high-density regions in interstellar dense molecular clouds (*cf.*, Pudritz and Fich, 1988). As a result, regardless of their original formation site, materials that end up in a newly

formed planetary system must have spent at least some time in the dense cloud environment. Molecular clouds are comprised of a mixture of gas and dust at very low temperatures (<30 K). At these temperatures, essentially any molecule hitting a dust grain will freeze out of the gas phase (*cf.*, Greenberg, 1978, 1982; Sandford and Allamandola, 1993a). Evidence for this process is found in the large quantities of mixed-molecular ices (*cf.*, Allamandola and Sandford, 1988) and gas-phase depletions (*cf.*, Mauersberger *et al.*, 1992) found in dense clouds. This process is very efficient; so efficient that even the universe's most volatile molecule, H_2 , suffers some loss from the gas phase in the presence of cold interstellar grains (Sandford *et al.*, 1993). Thus, the products of gas-phase chemistry in the interstellar medium should spend most of their lifetimes in icy grain mantles.

The composition of the ice mantles is not expected to simply reflect gas-phase abundances, however. Instead, additional species will also be formed when condensing species participate in gas-grain reactions on the grain surfaces, reactions that cannot occur solely in the gas phase (*cf.*, Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985; Brown and Charnley, 1990; Hasegawa *et al.*, 1992). The compositions of these new species will depend largely on the local H/H_2 ratio. In environments where the H/H_2 ratio is large, surface reactions with H atoms are important and atoms like C, N, and O will be converted to simple hydrides like CH_4 , NH_3 , and H_2O . If the H/H_2 ratio is substantially <1 , reactive species such as O and N are free to react with one another forming molecules such as O_2 and N_2 . Thus, two qualitatively different types of ice mantle may be produced by grain surface reactions, one dominated by polar, H-bonded molecules and the other dominated by nonpolar or only slightly polar, highly unsaturated molecules (see Figs. 4a,b). These two types of mantle could potentially exist simultaneously in different zones within a given cloud or might exist sequentially in the same portion of a cloud as it evolves.

Gas-grain chemistry is also expected to produce large D-enrichments in the grain mantles (Tielens, 1983, 1992). As with the ion-molecule gas-phase reactions, the enrichment is the result of mass fractionation effects that become significant at the extremely low temperatures typical of interstellar clouds. Models indicate that the D-enrichments generated in this fashion can attain mantle D/H ratios as high as 0.1, values which meet or exceed the enrichments observed in gas-phase species like $\text{DCO}^+/\text{HCO}^+$ that are presumably produced by ion-molecule reactions. Since the grain mantles in dense clouds generally represent a much larger fraction of the total reservoir of material than does material in the gas phase, grain surface processes may actually be far more important for the total D fractionation in dense clouds than ion-molecule reactions.

The interested reader is encouraged to see Tielens and Hagen (1982), d'Hendecourt *et al.* (1985), Williams (1987a,b), Brown and Charnley (1990), Sandford and Allamandola (1993a), and references therein for more detailed discussions of the astrochemical consequences of condensation and gas-grain chemistry processes.

Irradiation and Thermal Processing of Interstellar Ices

Interstellar ices are expected to be further modified by energetic processing by ambient ultraviolet radiation and cosmic rays (Greenberg, 1976; Norman and Silk, 1980; Prasad and Tarafdar, 1983). When these ices are irradiated, bonds are broken, molecules are destroyed, and new molecules, radicals, and other molecular fragments are formed (Fig. 4c). At the low temperatures characteristic of dense interstellar clouds, some of these reactive species are trapped and stored in the ice matrix. The accumulation of such

GRAIN MANTLE GROWTH AND EVOLUTION

GRAIN SURFACE REACTIONS PRODUCE "SIMPLE" MOLECULAR MANTLES

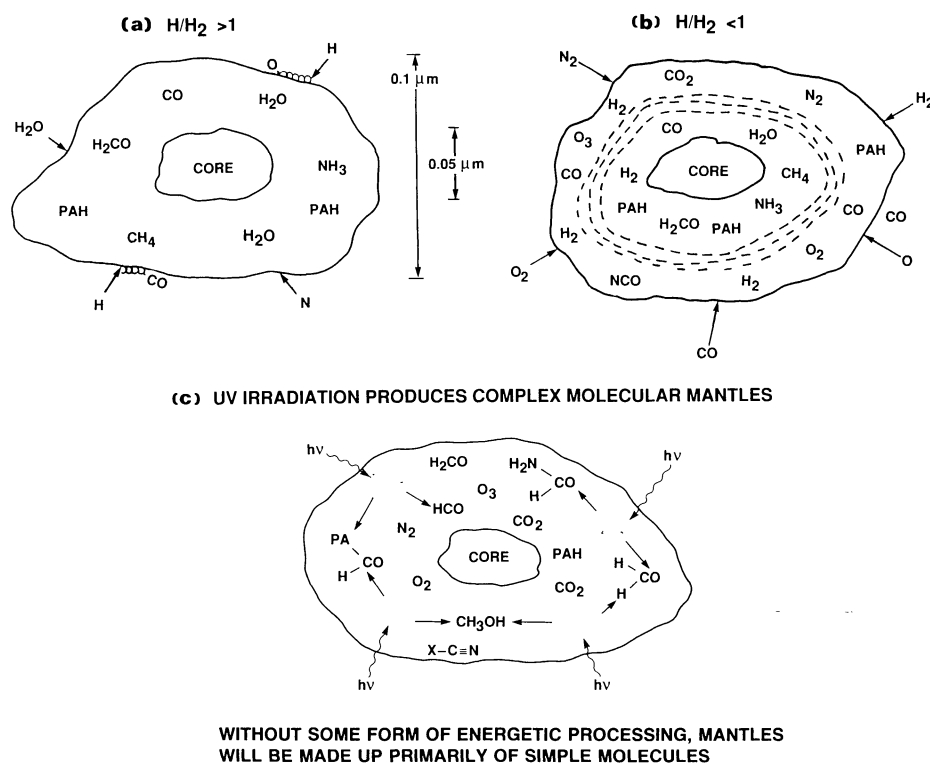


FIG. 4. Schematic drawings of the types of mantles expected to be present on the dust in dense molecular clouds. (a) In regions where the local H/H_2 ratio is large, various atomic and molecular species will accrete from the gas phase. Accreted H is sufficiently mobile that it can "hop" along the surface of the grain and react with other accreted atoms and molecules. As a result, simple hydrides like CH_4 , NH_3 , and H_2O will dominate. (b) In contrast, low H/H_2 ratios result in the production of mantles rich in H-deficient species like CO, O_2 , and N_2 . (c) Irradiated and thermal processing of ice mantles creates more complex molecular species and can result in the production of more refractory "organic" mantles.

reactive species will ultimately be interrupted by a thermal event (such as the passage of a shock wave, a grain-grain collision, cosmic-ray interaction, or exposure to a stellar system) that causes the ice to warm to the point at which molecular fragments can become mobile, react, and form new molecular species, many of them quite complex. Thus, an additional population of species formed by the irradiation and thermal processing of ices is expected to be present (*cf.*, Moore *et al.*, 1983; Agarwal *et al.*, 1985; Allamandola *et al.*, 1988; Shalabiea and Greenberg, 1994; Bernstein *et al.*, 1995). During thermal events, some of the new molecules formed in and on the grains will reenter the gas phase where they can be detected by radio techniques.

Evidence that grain-related processes do, in fact, occur is provided by the observation that many ices and gas-phase molecules identified in the ISM cannot be explained solely in terms of simple gas-phase chemistry models. Recent models that include contributions from gas-grain interactions and photochemical reactions appear to be more successful at explaining many of the species seen in dense clouds (*cf.*, Charnley *et al.*, 1992; Tegler *et al.*, 1993).

GASES AND SOLIDS IDENTIFIED IN THE INTERSTELLAR MEDIUM

In general, dust in the diffuse interstellar medium is believed to consist of mixtures of silicate and carbonaceous materials (*cf.*,

Mathis *et al.*, 1977; Greenberg, 1978; Jones *et al.*, 1987). In more benign environments, this material is augmented by gas-phase molecules and ices (Allamandola and Sandford, 1988; van Dishoeck *et al.*, 1993). The evidence for these various materials in the ISM will be reviewed in the following sections. Additional recent reviews of interstellar dust models and grain populations can be found in Allamandola (1984), Tielens and Allamandola (1987), Greenberg (1989), Mathis (1989), Williams (1989), and Sandford (1996).

Gas-Phase Molecules

As mentioned earlier, radio spectral techniques have demonstrated that dense molecular clouds contain a large variety of gas-phase molecules. This population contains both simple molecules like CO, OH, and CN and more complex species like HC_9N . There can be no doubt that the actual interstellar population contains far more species than the ~100 so far identified. These include species whose rotations don't produce oscillating dipole moments, large molecules whose rotation lines are so closely spaced that their transitions fall in other spectral regions, and, of course, species whose abundances fall below current detection limits.

The overall gas-phase population most likely originates from the interplay of gas-phase chemistry (*cf.*, Herbst, 1987) and grain chemistry (*cf.*, Charnley *et al.*, 1992; Bernstein *et al.*, 1995). For reviews of the molecules so far identified in space using radio techniques, the reader is invited to see Mann and Williams (1980), Irvine and Hjalmarsen (1984), and van Dishoeck *et al.* (1993), the last of which contains a table giving a recent summary of identified molecules.

One of the more abundant families of gas-phase species not detected by radio techniques are polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons are large planar molecules consisting of fused hexagonal rings of C having H on their peripheral rings. They tend to have small dipole moments (if any at all) and, because of their size, have rotation lines that are too closely spaced to be amenable to detection in the radio. Since PAHs currently represent one of the "hotter" topics in astronomy, I cannot possibly review in this paper the tremendous progress made in this field over the last ten years. Instead I provide a brief summary of the evidence for gas-phase PAHs in the ISM and touch on several areas of particular interest to meteoriticists. Readers interested in pursuing this field in more detail are referred to several excellent reviews already in existence (Allamandola *et al.*, 1989a; Puget and Leger, 1989; Allamandola, 1991).

Polycyclic aromatic hydrocarbons and related aromatic materials were originally suggested as candidates for the carriers of the

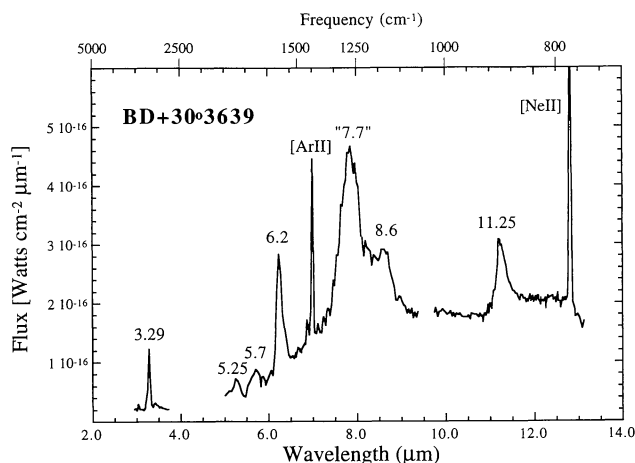


FIG. 5. The 3300–770 cm^{-1} (3.0–13.0 μm) spectrum of BD+30°3639, a compact planetary nebula. With the exception of the (ArII) and (NeII) atomic lines, the infrared emission from this object is thought to come from polycyclic aromatic hydrocarbons (PAHs) excited by UV radiation. The features are most likely associated with the following vibrations: 3040 cm^{-1} (3.29 μm), C-H stretch; 1905 cm^{-1} (5.25 μm), combination/overtone of C-H bends; 1750 cm^{-1} (5.7 μm), combination/overtone of C-H bends or C=C stretch; 1615 cm^{-1} (6.2 μm), C=C stretch; "1300" cm^{-1} (7.7 μm), C=C stretch; 1150 cm^{-1} (8.7 μm), C-H in-plane bend; 890 cm^{-1} (11.25 μm), C-H out-of-plane bend. (The figure is a composite of unpublished data of the author's and data from Allamandola *et al.*, 1989b and Witteborn *et al.*, 1989.)

family of infrared emission features seen in the spectra of a variety of planetary nebulae, reflection nebulae, and H II regions, which are all environments rich in UV radiation (Fig. 5) (Duley and Williams, 1981; Leger and Puget, 1984; Allamandola *et al.*, 1985). The narrower emission features are thought to be produced when free molecular PAHs absorb UV photons and cool by emitting a cascade of infrared photons while the broader underlying emission structure may be due to PAH clusters or amorphous carbons rich in aromatics. Polycyclic aromatic hydrocarbons are relatively large molecules and they contain a large number of vibrational modes in which to store absorbed energy. In addition, their conjugate π bonds make them particularly stable. Thus, although most molecules would be destroyed by UV photons under these conditions, PAHs can survive in the interstellar radiation field by virtue of their size and stability. A great deal of subsequent laboratory and astronomical work indicates that the basic suggestion that aromatic materials are responsible for the interstellar infrared emission is correct. Depending on the local environment, the total emission may include contributions from PAH neutrals, PAHs with chemical side groups, PAHs incorporated into grains, and PAH cations (which probably dominate the spectrum) (Schutte *et al.*, 1993a; Allamandola *et al.*, 1995; Joblin *et al.*, 1996).

Fluorescence from PAHs may also be a contributor to the Extended Red Emission (ERE) seen in many of the same objects that produce the infrared emission features, although another type of aromatic material, Hydrogenated Amorphous Carbon (HAC), is likely to be responsible for most of the ERE. The ERE is characterized by broad emission that extends from ~5500 to 8500 Å and peaks in the 6600–6800 Å region (*cf.*, Witt and Schild, 1988; Furton and Witt, 1992). There appears to be a size distribution of species that contribute to this emission, starting with molecular species containing ~20 C atoms and extending up to small particles having >1000 C atoms. A discussion of the possible PAH contribution to the ERE can be found in d'Hendecourt *et al.* (1986a).

Polycyclic aromatic hydrocarbons may also help resolve one of the classic spectroscopic problems of the 20th century, namely the identity of the carriers of the diffuse interstellar bands (DIBs). The presence of weak absorption features in the visible portion of the spectrum due to material in the diffuse ISM has been known since the detection of the first bands over seven decades ago (Heger, 1921; Trumpler, 1930). Since that time, over a hundred different DIBs have been identified (*cf.*, Krelowski, 1988; Herbig and Leka, 1991; Jenniskens and Desert, 1994; Herbig, 1995), and yet not a single band has had its carrier unequivocally identified. In 1985, PAH ions were suggested as possible carriers (Allamandola *et al.*, 1985; van der Zwet and Allamandola, 1985; Leger and d'Hendecourt, 1985), and subsequent laboratory studies have confirmed their viability as potential carriers of at least some of the bands (see Allamandola, 1995 and Salama *et al.*, 1995 for reviews).

Interestingly enough, the smallest members of the PAH family are expected to become D-enriched as a result of unimolecular photodissociation. As mentioned above, PAHs are generally quite hardy with regard to surviving the capture of a UV photon. However, if a PAH absorbs a photon that contains more energy than it can safely accommodate vibrationally, a bond or bonds will break. The single most likely bond to break is that of a peripheral C-H. Because of the zero-point energy difference in the strength of the C-D bond with respect to the C-H bond, the rate of D loss from interstellar PAHs should be lower than the loss of H. Since both H and D will return to this molecular site from the gas phase, one would expect PAHs to gradually become D-enriched relative to the ambient gas (Allamandola *et al.*, 1987, 1989a). This process has some interesting consequences. First, unlike ion-molecule or gas-grain reactions, very low ambient temperatures are not required to produce fractionations by this process. Second, the extent of the D-enrichment depends critically on the size of the PAH. The photoenrichment of D in PAHs is expected to be most significant for PAHs in the range of sizes spanned by naphthalene (C_{10}H_8 , C/H = 1.25) and hexabenzocoronene ($\text{C}_{42}\text{H}_{18}$, C/H = 2.33). Deuterium enrichment is not expected in benzene because this molecule is not stable in the interstellar radiation field. Enrichment in PAHs having >~40 C atoms is not expected because these molecules have large numbers of vibrational modes and are stable against photolytic bond rupture. With this in mind, it is interesting to note that a significant fraction of the D in meteorites appears to be carried by aromatics (Kerridge *et al.*, 1987). In addition, the D/H ratio of acid-soluble hydrocarbon phases in meteorites increases as C/H increases from 0.2 to 1.5 (Yang and Epstein, 1983) while the D/H ratio in acid insoluble phases drops slightly as the C/H ratio increases from 2.3 to 3.0 (Robert and Epstein, 1982). If we assume that the soluble and insoluble phases represent different degrees of molecular complexity of related materials (which is likely to be a gross oversimplification), then the D-enrichment peaks at a C/H of ~2, a value that implies the dominance of aromatics over aliphatics. A C/H ratio of ~2 would correspond to PAHs containing 20 to 50 C atoms, which is the same size range inferred to be most abundant in the ISM and most likely to be enriched by unimolecular photodissociation. While the preceding argument is clearly overly simplistic, it does demonstrate that interstellar PAHs should be seriously considered as significant carriers of D-enrichments in meteorites.

Refractory Grains (Silicates, Silicon Carbide, Oxides, Graphite)

There is spectral evidence for the existence of a number of refractory solids in the ISM. These include silicates, silicon carbide, oxides, and graphite. The identification of silicates and SiC are

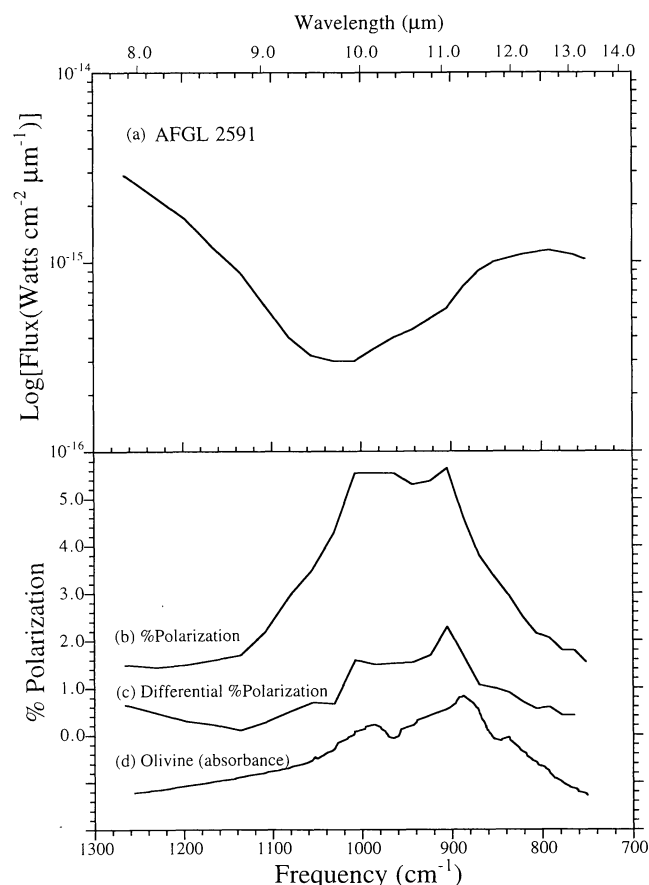


FIG. 6. (a) The "10 μm " silicate absorption feature seen in the spectrum of the embedded astronomical object AFGL 2591. (b) The percent polarization measured across the silicate absorption feature. (c) The excess polarization resulting when the polarization shown in (b) is normalized to the "standard" featureless polarization feature of the Becklin-Neugebauer object. (d) The absorption spectrum of a Guadalupe Ultramafic Xenolith olivine standard. The striking similarity of the bottom two traces suggest that crystalline olivine may be present along the line-of-sight to AFGL 2591. (The AFGL 2591 data are from Aitken *et al.*, 1988; the olivine spectrum was taken by the author.)

fairly secure, but little is currently known about the compositional or crystallographic nature of these materials. The identifications of oxides and graphite are more tentative.

Silicates—The strongest evidence for the presence of silicates in space comes from the detection of infrared features near 1030 and 525 cm^{-1} (9.7 and 19 μm) in the spectra of a variety of interstellar objects (Fig. 6a). These bands are often referred to as the "10" and "20" μm features, respectively. These features are seen in both absorption (*cf.*, Willner *et al.*, 1982; Roche and Aitken, 1984; Whittet *et al.*, 1988) and emission (*cf.*, Treffers and Cohen, 1974; Merrill and Stein, 1976; Knacke *et al.*, 1993; Sloan and Price, 1995) and their positions are characteristic of Si-O stretching and Si-O-Si bending mode vibrations in silicates (Farmer, 1974a).

It is often difficult to determine whether the observed features are due to silicate grains along the line-of-sight to the observed object (*i.e.*, the grains are truly interstellar) or whether the grains are associated with the star being observed (*i.e.*, are circumstellar). Features seen in emission are most likely due to circumstellar grains heated by a nearby star and, thus, are probably not strictly due to

interstellar dust. The situation is usually less clear when the feature is seen in absorption.

The "10 μm " silicate absorption band is perhaps the most ubiquitous infrared spectral feature seen along lines-of-sight that pass through interstellar dense molecular clouds (Willner *et al.*, 1982; Roche and Aitken, 1984; Whittet *et al.*, 1988). This feature is generally one of the two strongest absorption bands in the spectrum (the other being the H_2O ice feature near 3250 cm^{-1}). These features are probably largely produced by dense cloud material but may include some spectral confusion from contributions by dust local to the infrared source (Fig. 3).

The better measured features generally have very little spectral fine structure, the main exception being that many of the band profiles show a weak "elbow" near 890 cm^{-1} (11.2 μm) on the low frequency wing of the silicate feature (Fig. 6a). Crystalline silicate minerals produce infrared features with distinctive substructure that differs from mineral to mineral (Farmer, 1974a; Sandford, 1984). The lack of strong spectral structure in the astronomical data, in conjunction with the observation that the intrinsic strength of the interstellar Si-O stretching band appears to be a factor of 2 to 3 \times smaller than that typical of well-crystallized minerals (Martin, 1975), suggests that the silicates in space are largely amorphous (see Whittet, 1988).

The source of the 890 cm^{-1} "elbow" is not presently clear. In several cases where it has been possible to obtain good quality spectropolarimetry data (Aitken *et al.*, 1988, Fig. 6b), the polarization peaks near the elbow and the frequency-dependent profile of the excess polarization amplitude is remarkably similar to the absorption band profile of crystalline olivine (Fig. 6c,d). This suggests that at least a portion of the silicates contain some structural order. Further support for the possibility that interstellar silicates may not be completely amorphous comes from the spectral database obtained by the Low Resolution Spectrometer (LRS) on the Infrared Astronomical Satellite (IRAS). The emission spectra taken from stars surrounded by *circumstellar* dust often show significant variations in the shape of the silicate feature. Analysis of these variations suggests that at least 5 independent spectral components are indicated (Tielens, 1990). These variations are most likely due to silicate grains having different compositions and degrees of crystallinity.

The presence of at least some crystalline silicates in the ISM should not come as a surprise since amorphous or "glassy" silicates are metastable and are susceptible to annealing processes on rapid time scales, even at relatively modest temperatures (*cf.*, Nuth *et al.*, 1986). Thus, the observed variations in circumstellar emission profiles and interstellar absorption polarimetry profiles may be due to a fraction of the dust that has experienced some form of heating episode.

It is interesting to note that the infrared spectra of some comets contain "10 μm " silicate emission features that also show spectral fine structure, including a distinct subfeature near the 890 cm^{-1} "olivine" position (*cf.*, Bregman *et al.*, 1987; Hanner *et al.*, 1994). Where seen, this subfeature is considerably stronger relative to the overall silicate emission feature than that seen in any of the interstellar spectra. This suggests that comets may contain a higher proportion of crystalline silicates than found in dust in the general ISM. Given that most interstellar materials will likely have experienced significant warming when entering the early solar nebula, the presence of a higher proportion of crystalline silicates in comets would not be surprising. Additional evidence for increased crystallinity in silicates incorporated into stellar systems comes from recent studies

that show that the dust in the disk around the star β Pictoris also produces a "10 μm " silicate feature that contains excess emission near 890 cm^{-1} (Knacke *et al.*, 1993).

It should be noted, however, that silicates are not the only possible source of the "elbow" near 890 cm^{-1} . The "elbow" could also be due to absorption from interstellar PAHs or other aromatic species. One of the stronger bands produced by PAHs falls near 890 cm^{-1} (see Fig. 5; Allamandola *et al.*, 1989a; Witteborn *et al.*, 1989). This feature is associated with C-H out-of-plane bending mode vibrations. Absorption by these modes are immensely enhanced in PAHs in the solid state (Witteborn *et al.*, 1989), so it is possible that the "elbow" could be due to aromatic materials, either in independent grains or in mixed carbon-silicate grains. Since aromatic materials are seen in close proximity to silicates in meteorites and interplanetary dust particles (*cf.*, Allamandola *et al.*, 1987; Tingle *et al.*, 1991; Kovalenko *et al.*, 1992; Clemett *et al.*, 1993), the suggestion has some merit. Unfortunately, this possibility has yet to be fully addressed.

The "10 μm " silicate feature has also been detected in the spectra of sources along lines-of-sight that pass through dust in the diffuse ISM (*i.e.*, in the intercloud medium; Roche and Aitken, 1985). The optical depth of the silicate feature seen towards these objects increases fairly linearly with visual extinction, which is consistent with a carrier located in the diffuse ISM (Fig. 7). There are indications that the spectral profile of the silicate feature produced by dust in the *diffuse* ISM may be measurably different from that produced by dust in the *dense* ISM. Comparison of the silicate features seen in the Taurus dense cloud medium and along the line-of-sight to the Galactic Center suggests that the former are better fit by a "Trapezium" emissivity function, while the latter is better fit by a " μ Cephei" emissivity function (Roche and Aitken, 1985; Whittet *et al.*, 1988). However, the assumed profile of the diffuse ISM silicate feature is largely based on the relatively limited number of diffuse ISM spectra associated with the Galactic Center. It is not presently clear if this difference holds for other lines-of-sight through the diffuse ISM, nor is it presently clear what the significance of the difference is.

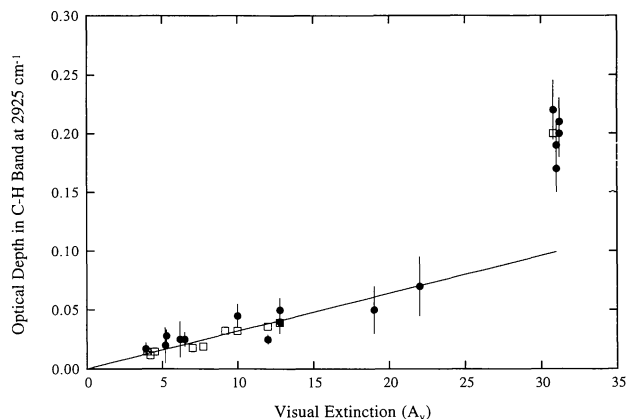


FIG. 7. Visible extinction (A_v) vs. the optical depth of the C-H and Si-O stretching bands of dust in the diffuse ISM. The filled circles are the optical depths of the 2925 cm^{-1} ($3.42\text{ }\mu\text{m}$) $-\text{CH}_2-$ band (Sandford *et al.*, 1991; Pendleton *et al.*, 1994). The open squares are the optical depths of the silicate band near 1000 cm^{-1} ($10\text{ }\mu\text{m}$) (Roche and Aitken, 1985). The silicate optical depths have been scaled by a factor of $1/13$ to normalize them to the strength of the 2925 cm^{-1} $-\text{CH}_2-$ feature at the Galactic Center. (Points associated with different sources in the Galactic Center have been slightly offset from each other in A_v for clarity.) (Figure adapted from Sandford *et al.*, 1995.)

Silicon Carbide—The detection of SiC in the ISM should be of particular interest to meteoriticists since SiC grains bearing isotopic signatures of a presolar origin have been found in meteorites (Bernatowicz *et al.*, 1987; Zinner *et al.*, 1987; Lewis *et al.*, 1989, 1990, 1994; Amari *et al.*, 1992; Virag *et al.*, 1992; Hoppe *et al.*, 1993). The isotopic and elemental evidence indicates that the meteoritic grains are largely the products of AGB stars during the C-rich phase of their evolution, although a small fraction could be from supernovae (*cf.*, Anders and Zinner, 1993; Amari *et al.*, 1995). The isotopic evidence for an origin in late-type, C-rich stars is consistent with the expected condensation products of such stars (*cf.*, Draine, 1981).

The strongest infrared band produced by SiC is associated with the Si-C stretching vibration and falls near 850 cm^{-1} ($11.8\text{ }\mu\text{m}$; Borghesi *et al.*, 1983). (Silicon carbide has no strong equivalent to the $19\text{ }\mu\text{m}$ silicate bending mode feature.) It is encouraging that a feature centered near this position has been detected in emission in the spectra of a number of C-rich stars (Fig. 8a; Treffers and Cohen, 1974; Merrill and Stein, 1976; Little-Marenin, 1986; Baron *et al.*, 1987; Whittet *et al.*, 1990). The observed feature extends from ~ 1000 to 800 cm^{-1} (10.0 – $12.5\text{ }\mu\text{m}$), a width that matches reasonably well with laboratory spectra of SiC. However, the astronomical feature peaks nearer 870 cm^{-1} ($11.5\text{ }\mu\text{m}$). The source of the mismatch in position is not clear but may be due to thermal emission or grain size distribution effects, differences in the degree of crystallinity, or a combination of these. To the best of my knowledge, this issue has yet to be rigorously addressed and its resolution will probably require measurement of additional laboratory spectra and more thermal emission modeling. There is some tantalizing evidence that the astronomical SiC feature contains some substructure. Thus, additional telescopic spectra taken at higher spectral resolution and signal-to-noise may also be very instructive. Spectropolarimetry measurements like those used by Aitken *et al.* (1988) for the silicate feature might also be useful.

The fact that the astronomical SiC feature has always been seen in emission suggests that the grains being observed are circumstellar, not interstellar. To date, I am unaware of any clear detection of SiC in the general ISM. Whittet *et al.* (1990) used the nondetection of SiC absorption in the diffuse ISM to derive an abundance limit and concluded that the column density of Si in interstellar SiC is no more than $\sim 5\%$ that in silicates. This upper limit is based on the assumption that the SiC grains in the ISM are small enough to be optically thin. The size range of SiC grains found in meteorites extends up to grains at least as large as $6\text{ }\mu\text{m}$ in diameter (Amari *et al.*, 1994), a size at which the grains may start to become optically thick. Thus, the 5% upper limit may be slightly underestimated. The interstellar SiC found in meteorites makes it clear that these grains do travel from their stellar production sites to locations where new stellar systems are formed. Thus, the general ISM, dense and diffuse, must contain some SiC. Presumably the lack of SiC detection in the ISM is due to a relatively low absolute abundance, while its detection in circumstellar sites is aided by higher local densities and favorable conditions. In any event, it should be kept in mind that the SiC so far observed telescopically most likely represents a "fresh," newly-formed population that has yet to suffer the rigors of the interstellar environment, and the emission may contain significant contributions from SiC grains not represented in the meteoritic collections.

Oxides—The issue of the presence of oxides in the ISM has taken on added importance since the recent detection of interstellar

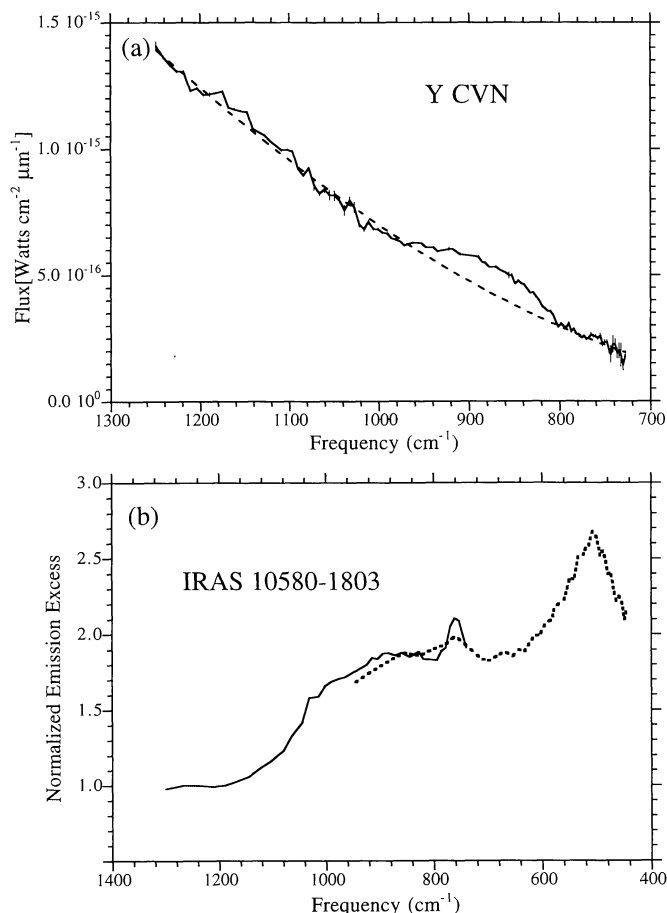


FIG. 8. The infrared spectra of stellar objects showing possible SiC and oxide emission features. (a) The 1300–700 cm^{-1} (7.7–14.3 μm) emission spectrum of the C-rich star Y CVN. The dashed line is an exponential fit to the local thermal continuum. The excess emission above the dashed line between 980 and 800 cm^{-1} (10.2–12.5 μm) is thought to be due to SiC. (Previously unpublished spectrum obtained by the author.) (b) The excess emission seen in the spectrum of the O-rich star IRAS 10580-1803 after removal of the underlying thermal continuum. The solid and dashed lines are from the high- and low-frequency scan ranges of the IRAS LRS instrument, respectively. This object falls in the metaclass $\lambda 34;4$ according to the classification scheme presented in Cheeseman *et al.* (1989). The excess emission features near 870, 765, and 510 cm^{-1} (11.5, 13.1, and 19.7 μm) have been identified with the presence of some form of oxide material. (Unpublished spectrum provided courtesy of J. Goebel.)

corundum (Al_2O_3) in meteorites (Huss *et al.*, 1994; Hutcheon *et al.*, 1994). The large ^{17}O excesses and high $^{26}\text{Mg}^*/^{27}\text{Al}$ ratios seen in the meteoritic grains are characteristic of H-burning nucleosynthesis and suggest that the grains were made in red giant or AGB stars as they pass through a Mira-variable stage having $\text{C/O} < 1$.

A host of simple oxide molecules like ZrO , TiO , ScO , VO , *etc.*, have been detected in the atmospheres of cool M- and S-type stars (Tsuji, 1986). The detection of oxide grains in space has proven to be more problematic. This is perhaps not surprising given the relative rarity of the meteoritic corundum. The positions and strengths of the infrared bands produced by oxide minerals depend strongly on the cations present (*cf.*, White and DeAngelis, 1967; Farmer, 1974b). However, as a general rule, they tend to produce a pair of bands or systems of bands that fall between 750 and 400 cm^{-1} (13 and 25 μm) for the more cosmically abundant cations. In the case of Al_2O_3 , these two bands fall near 600 and 450 cm^{-1} (16.7 and 22.2 μm).

Data obtained by the Low Resolution Spectrometer (LRS) on the Infrared Astronomical Satellite (IRAS) provide some tentative evidence for this type of material in space (Fig. 8b). Cheeseman *et al.* (1989) used a Bayesian classification algorithm to categorize all the 5000+ spectra in the LRS database into "metaclasses" based on their spectral characteristics. They established the existence of a class (Class λ) containing a large number of sources that show evidence for emission features near 870, 765, and 510 cm^{-1} (11.5, 13.1, and 19.7 μm) in addition to the well-known "10 μm " silicate feature. Of the sources in this class that have been previously identified, most are O-rich, cool M-type giants and Mira variables. Since the features are always seen in emission, the grains responsible are probably circumstellar, not interstellar.

In an independent study, Little-Marenin and Little (1990) classified the spectra of the M-type Mira variable stars in the LRS database and established a grouping that essentially reproduces that of Cheeseman *et al.*'s Class λ . Little-Marenin and Little suggested that the 870 and 510 cm^{-1} features were due to crystalline olivine since its two strongest bands fall near these locations. However, Goebel *et al.* (1989) have noted that the 765 and 510 cm^{-1} features were strongly correlated, even in cases where the "10 μm " silicate peak is absent. They suggested instead that the 765 and 510 cm^{-1} are due to metal oxides rather than silicates. More recently, in an additional search of the LRS database, Sloan *et al.* (1996) concluded that the 765 cm^{-1} feature might be related to $\alpha\text{-Al}_2\text{O}_3$ and noted that 40–50% of all O-rich AGB stars and 75–90% of SRb variables show the feature.

Unfortunately, no single oxide mineral seems to produce a spectrum that provides a good fit to the astronomical features. I have compared a large number of lab spectra of oxides and related materials (both published spectra and those I have obtained myself) and have yet to find a good fit. Nonetheless, the general form and behavior of the telescopic spectra of these stars is similar to oxide materials. At this point it is not clear whether the lack of a good match is due to the rather limited resolution and signal-to-noise of the LRS spectra, spectral confusion from the overlap of bands from many different minerals (including oxides), the presence of oxides having different compositions or degrees of crystallinity from those studied in the laboratory, or the complete absence of oxides. In summary, there have been no unequivocal identifications of oxides in the ISM to date, although possible circumstellar candidates do exist. The fact that the candidate features are seen in the spectra of the same types of stars that are inferred to be the sources of the meteoritic corundum grains is encouraging, and it can be hoped that future infrared observations of these stars will clarify the identification of oxides.

Graphite—Graphite has long figured prominently in the discussion of materials in the ISM. It is a common component used in theoretical models that attempt to explain the shape of the interstellar extinction and polarization curves across the infrared, visible, and ultraviolet (*cf.*, Mathis *et al.*, 1977). The principal motivation for invoking crystalline graphite as a grain constituent is that it is one of the better candidate materials for producing the infamous 2175 Å extinction feature (see Draine, 1989 for a review of the possible candidates). Part of the appeal of graphite has undoubtedly also been that it is one of the few carbonaceous materials that is well characterized and for which good laboratory optical constants are available (*i.e.*, its use has been driven to some extent by computational considerations rather than by any motivation associated with its clear detection in the ISM).

There is presently no infrared spectral evidence for the presence of graphite in the ISM. This is due in large part to the very nature of graphite. Since crystalline graphite has a high degree of molecular symmetry and consists of only one element, most of its vibrational modes produce little or no change in dipole moment. As a result, graphite has few modes that are "infrared-active" and produces no strong spectral features. From the optical properties of graphite obtained by Nemanich *et al.* (1977) using infrared reflectance and Raman spectroscopy, Draine (1984) calculated that small graphite grains should produce a weak, narrow feature near 868 cm^{-1} ($11.52\text{ }\mu\text{m}$) and an even weaker one near 1590 cm^{-1} ($6.30\text{ }\mu\text{m}$). A subsequent search made by Glasse *et al.* (1986) specifically for the 868 cm^{-1} band in the spectrum of the C-rich WC9 star Ve 2-45 failed to detect a feature. In addition, this feature has not been seen in a substantial number of spectra of other C-rich objects taken for other reasons. Unfortunately, there has never been a concerted effort to use the available (or new) data to derive careful quantitative upper limits for the abundance of graphite in the ISM. Given the weakness of the graphite features, their nondetection could still be consistent with the presence of a substantial amount of graphite. Draine (1989) notes that having $\sim 15\%$ of cosmic C in the form of graphite is all that is needed to reproduce the $2175\text{ }\text{\AA}$ feature, and I doubt that any of the available infrared data provides upper limits this tight.

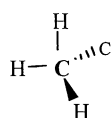
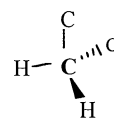
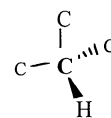
Modelers of the interstellar extinction were understandably excited when interstellar graphite grains were discovered in meteorites (*cf.*, Amari *et al.*, 1990; Zinner *et al.*, 1995). This excitement was tempered somewhat by the fact that the meteoritic grains are not the small, abundant, perfectly crystallized graphite particles used in most models. Instead, the meteoritic grains show several morphological types, often contain concentric scales of more poorly graphitized C, and account for only a minor fraction of the C inventory in meteorites (Nuth, 1985; Bernatowicz *et al.*, 1991; Zinner *et al.*, 1995). However, it had already been noted that the observed variations in the profile of the interstellar $2175\text{ }\text{\AA}$ extinction feature cannot be explained solely in terms of variations in the grain size, shape, clumping, or coating of crystalline graphite (*cf.*, Draine and Malhotra, 1993). Instead, the range of observed features seemed to require variations in the dielectric properties of the grains themselves (*i.e.*, the interstellar graphite must contain impurities or have varying degrees of crystallinity). The meteoritic graphite grains provide clear evidence of this and it can be hoped that the meteoritic grains will be used to guide the construction of additional future interstellar extinction models that consider the implications of more realistic graphitic materials.

Despite the general satisfaction of having the meteoritic and astronomical evidence both point to a similar material, comparison of the meteoritic graphite with the inferred interstellar graphite raises some important questions. The inferred interstellar graphite grains must be small (radii $\leq 150\text{ }\text{\AA}$) if they are to explain the $2175\text{ }\text{\AA}$ extinction feature (Draine, 1989). In contrast, the graphite grains found in meteorites are enormously larger, typically having radii in the 1 to $5\text{ }\mu\text{m}$ range (Bernatowicz *et al.*, 1991; Zinner *et al.*, 1995). Thus, the meteoritic graphite grains and the "interstellar" graphite grains are not the same particles, and it cannot be assumed that the two simply represent different size end-members of the same grain population. Any continuous grain size distribution that attempts to explain the $2175\text{ }\text{\AA}$ feature and that extends up to sizes of $5\text{ }\mu\text{m}$ will quickly run into C abundance constraints. For example, if one assumes a common power law size distribution of the form $N(a) \propto a^{-3.5}$

(see Mathis *et al.*, 1977) and requires that $\sim 15\%$ of cosmic C be in the radius $\leq 150\text{ }\text{\AA}$ range to explain the $2175\text{ }\text{\AA}$ bump (Draine, 1989), one finds that $\sim 250\%$ of all the cosmic C needs to be in graphite! Obviously, the meteoritic grains do not represent the larger end members of a continuous, monotonic size distribution of graphite grains extending from $50\text{ }\text{\AA}$ to $5\text{ }\mu\text{m}$. There must be some sort of "gap" in the graphite size distribution between the "astrophysical" graphite grains and those found in meteorites. Thus, it is likely that the meteoritic graphite grains and interstellar "graphite" particles responsible for the $2175\text{ }\text{\AA}$ feature are *completely* unrelated. I will return to this point in the Discussion section of the paper where I will make a somewhat radical suggestion with regard to how the interstellar graphite question might best be addressed using the meteoritic data.

In summary, at this point it is fair to say that an explanation of the $2175\text{ }\text{\AA}$ feature using graphite is not ruled out by any observational constraints. However, if graphitic grains are responsible, they are not the same as those found in meteorites. Whether these two types of graphite are in any way related or whether they represent materials having completely different origins and evolutionary histories is not presently clear. Finally, we have no satisfactory handle on the real abundance of graphite in the ISM, although a lower limit of $\sim 15\%$ of the cosmic C abundance would seem to be required to explain the $2175\text{ }\text{\AA}$ feature.

Microdiamonds—During a search for CH_3OH bands in the spectra of dense molecular clouds, Allamandola *et al.* (1992) serendipitously detected a new, weak absorption feature near 2880 cm^{-1} ($3.47\text{ }\mu\text{m}$) in the spectra of 4 embedded objects (Fig. 9b). This feature falls on the wing of the " $3\text{ }\mu\text{m}$ " H_2O ice band at a position characteristic of C-H stretching vibrations. Its strength varies independently of the ice features seen in the same spectra, thus implying the carrier is not a volatile. Subsequent (unpublished) work by this group and others (Brooke *et al.*, 1995; Sellgren *et al.*, 1995) has shown that the feature exists in the spectra of virtually all dense clouds studied to date. The band falls at a unique position characteristic of the C-H stretch of tertiary carbon (*i.e.*, a C atom bonded to one H and 3 other carbons). The structure of a tertiary (3°) C is shown below in comparison with primary (1° , methyl) and secondary (2° , methylene) carbons.

primary (1°)secondary (2°)tertiary (3°)

The detection of a tertiary C feature, in conjunction with an absence of strong features due to primary ($-\text{CH}_3$) and secondary ($-\text{CH}_2-$) carbons, led Allamandola *et al.* (1992) to suggest that the carrier has a diamond-like structure. This suggestion would undoubtedly have been greeted with a great deal more skepticism had not meteoritic studies already provided ample evidence for the existence of interstellar microdiamonds (*cf.*, Lewis *et al.*, 1987; Blake *et al.*, 1988; Ming and Anders, 1988; Fraundorf *et al.*, 1989; Bernatowicz *et al.*, 1990). Some additional support for a diamond-like carrier comes from the detection of a weak band near 1350 cm^{-1} ($7.41\text{ }\mu\text{m}$) in the spectra of one of these objects (Lacy *et al.*, 1991). Hydrogen atoms bonded to diamonds produce a weak C-H bending vibration band near 1340 cm^{-1} ($7.46\text{ }\mu\text{m}$; Bellamy, 1960).

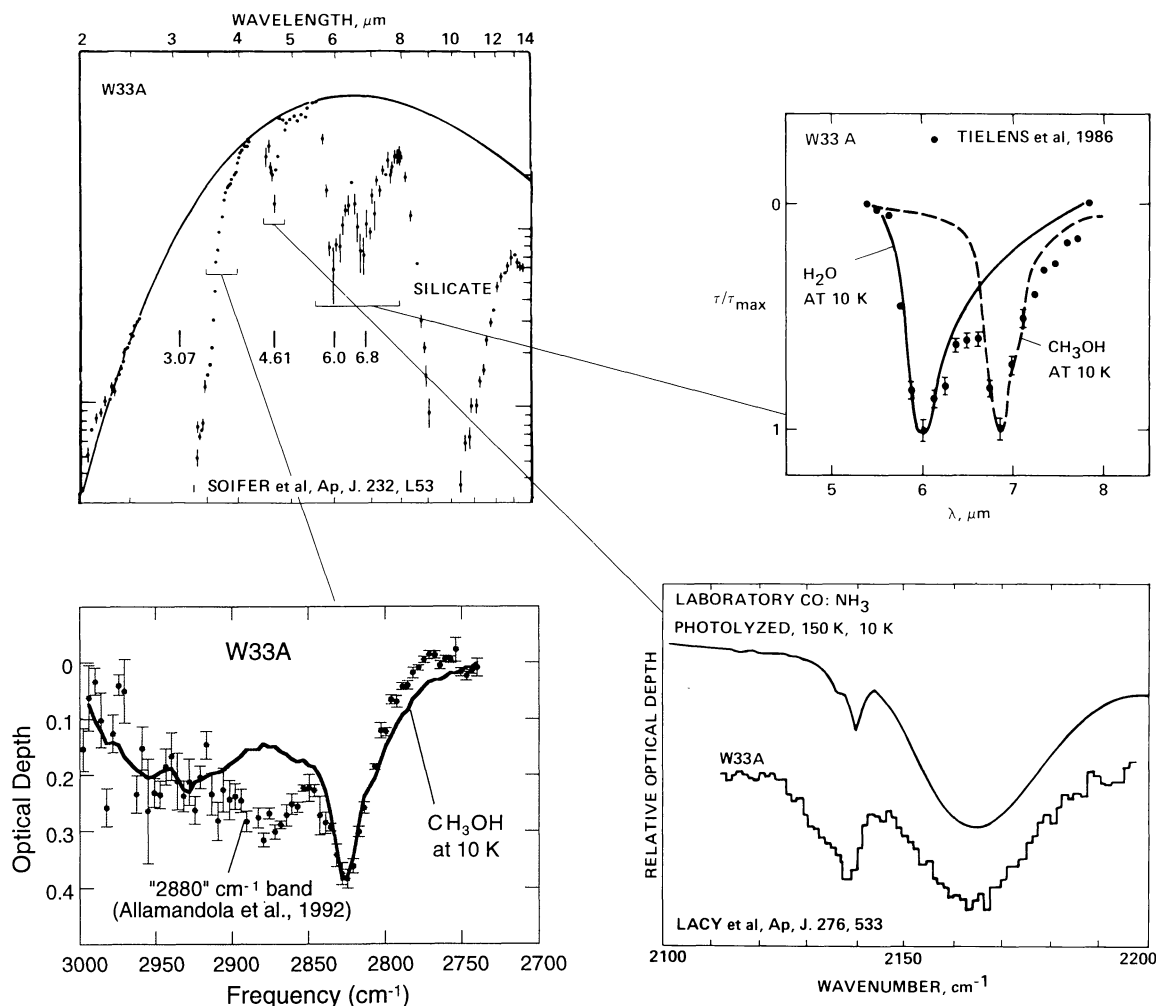


FIG. 9. Comparisons of laboratory spectra and spectra from the object W33A, a protostar embedded in a dense molecular cloud that produces ~50 to 100 magnitudes of foreground visual extinction. (Upper left) The overall spectrum of W33A from 5000 to 715 cm^{-1} (2.0–14.0 μm). The solid line corresponds to the quasi-blackbody emission spectrum thought to be produced by the protostar. Note the strong 10 μm absorption due to silicates. (Lower left) An expansion of the 3000 to 2700 cm^{-1} (3.3–3.7 μm) region. The solid line is the spectrum of a laboratory ice containing methanol. The "excess" absorption at 2880 cm^{-1} is thought to be due to hydrogenated surface atoms on microdiamonds. (Upper right) An expansion of the 2000 to 1250 cm^{-1} (5–8 μm) region. The solid and dashed lines are the spectra of laboratory H_2O and CH_3OH ices, respectively. (Lower right) An expansion of the 2200 to 2100 cm^{-1} (4.55–4.76 μm) region. The feature near 2140 cm^{-1} is due to solid CO and the feature near 2165 cm^{-1} is thought to be due to a $\text{C}\equiv\text{N}$ -containing compound.

It is difficult to precisely determine the abundance of this material in the ISM. Part of the uncertainty is due to the fact that the measured C-H stretching band is probably largely due to C atoms in the surface of the grain. The optical depth of the 2880 cm^{-1} band indicates that a minimum of ~5% of the available cosmic C must be tied up in this material (Allamandola *et al.*, 1992). However, C in the center of a classical diamond structure is bonded only to other carbons and its vibrations are infrared inactive. Thus, internal C atoms are largely invisible in the infrared (indeed, diamonds are often used as windows for infrared studies!). By assuming that the inferred interstellar microdiamonds have the meteoritic size distribution reported by Lewis *et al.* (1987), Allamandola *et al.* (1992) showed that the strength of the 2880 cm^{-1} feature implied that microdiamonds could account for as much as 20% of the total available cosmic C. However, later measurements indicate that the median size of the meteoritic microdiamonds is probably closer to ~10 Å (Fraundorf *et al.*, 1989) than the 26 Å mean reported by Lewis *et al.* Use of the smaller mean size would decrease the

inferred interstellar microdiamond abundance to closer to 10%. The highest abundances typically found in meteorites are on the order of a few percent of their total carbon (*cf.*, Huss and Lewis, 1995). These results suggest that microdiamonds are quite abundant in space and that they have a remarkable ability to survive the rigors of incorporation into small parent bodies formed in the early solar system. (Perhaps this is not a complete surprise since they are obviously tough enough to survive the abuses meteoriticists heap on them in the process of extracting them from the meteorites!)

Given their apparent hardy nature, one might expect the diamonds would also survive in the diffuse ISM. Unfortunately, it will be very difficult to unambiguously detect the 2880 cm^{-1} feature in absorption in the diffuse ISM due to spectral interference. Approximately 10% of the C in the diffuse ISM is in the form of $-\text{CH}_2-$ and $-\text{CH}_3$ groups in grains rich in aliphatic hydrocarbons (see the end of the next section). The intrinsic strength of the C-H stretching features of aliphatic hydrocarbons (per C atom) are 2 to 3 \times higher than that expected for microdiamonds. As a result, if microdia-

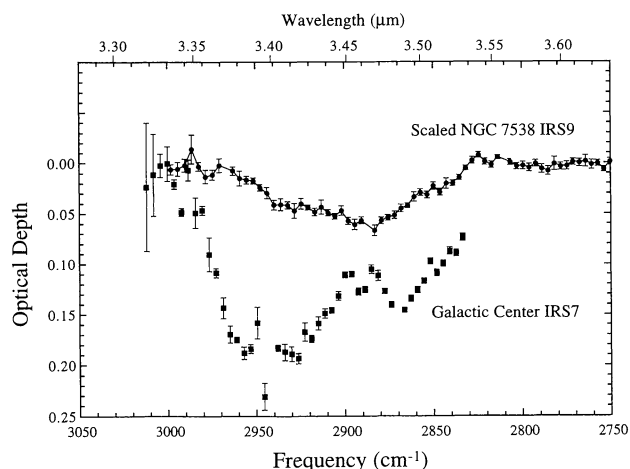


FIG. 10. The C-H stretching region spectra of NGC 7538 IRS 9 (representative of dust in the dense ISM) and of Galactic Center source IRS 7 (representative of dust in the diffuse ISM). The spectrum of NGC 7538 IRS 9 has been scaled in absorbance to match an A_V equivalent to that seen toward the Galactic Center. This comparison illustrates the unexpected, fundamental differences between the refractory organics in both media and demonstrates that microdiamonds could be present in the diffuse ISM as well as the dense ISM but have their spectral signature covered up by the stronger absorptions of $-\text{CH}_3$ and $-\text{CH}_2-$ groups in aliphatic materials. (Figure adapted from Allamandola *et al.*, 1993.)

monds are present in the diffuse ISM in the same abundances inferred for dense clouds, the microdiamond C-H feature is expected to be completely obliterated by the much stronger overlapping aliphatic features (Fig. 10). Indeed, the profile of the diffuse aliphatic feature is easier to match with aliphatic compounds if it is assumed that some microdiamond is present. At present, all that can be said from the C-H stretching band profiles in diffuse ISM spectra is that the presence of microdiamonds in the diffuse ISM is not inconsistent with the observed absorbances (Allamandola *et al.*, 1992).

As a speculative note along these lines, the spectra dominated by emission features assigned to polycyclic aromatic hydrocarbons sometimes contain a minor emission band near 2890 cm^{-1} ($3.46\text{ }\mu\text{m}$). This is one of the few features whose assignment has remained ambiguous within the framework of the PAH identification (Barker *et al.*, 1987; Sandford, 1991). Since the meteoritic interstellar diamonds span the same range of sizes as inferred for PAHs, they would experience very similar IR fluorescence processes upon UV photon absorption. Thus, it is possible that the 2890 cm^{-1} emission feature seen in the spectra of more diffuse regions could be associated with microdiamonds. If this is the case, the relative strengths of the emission features suggests that the smallest interstellar diamonds are typically somewhat larger ($N_C \approx 500\text{ C atoms}$) than the smallest PAHs (Allamandola *et al.*, 1992). This inferred size falls in the middle of the range determined from meteoritic microdiamonds (60–1100 atoms).

The ultimate source of the interstellar microdiamonds remains uncertain, although several formation processes, including chemical vapor deposition, photolysis of hydrocarbons, and grain collisions produced by interstellar shocks, have been suggested (see Anders and Zinner, 1993). Recent transmission electron microscope studies of the meteoritic microdiamonds suggest that formation by chemical vapor deposition is most likely (Daulton *et al.*, 1996). Unfortunately, since the 2880 cm^{-1} feature has only been detected in dense clouds and not in the local environments associated with potential sources, the spectral data provide little information about the source(s) of

this material. However, the ubiquity of the band in the spectra of dense clouds and the inferred high abundances of microdiamonds suggests that the formation involves a relatively common environment rather than an exotic one. (Several notes: contrary to the statement made in Anders and Zinner, 1993, Allamandola *et al.*, 1992, 1993 *do not* infer from their data that interstellar shocks are the most likely source for the microdiamonds. Instead, they simply point out that the ubiquity of this carrier suggests exotic formation sites are ruled out. Also, Anders and Zinner (1993) infer that microdiamonds are absent from the diffuse ISM and state that the major models suggested for the formation of interstellar diamonds all have difficulty explaining this. However, as noted above, present spectra of the diffuse ISM are perfectly consistent with the presence of the microdiamonds.)

Ices in Interstellar Dense Molecular Clouds

As discussed earlier, the condensation of gas-phase molecules onto grains is expected to be very efficient in dense molecular clouds, and most of the products of gas-phase chemistry in the ISM should spend the majority of their lifetimes in icy grain mantles. Additional species will also be formed when condensing species participate in gas-grain reactions on the grain surfaces or are subjected to irradiation and thermal processing. As discussed earlier, many of these processes are expected to enrich the mantles in deuterium.

Figure 3 provides a schematic of how the composition of interstellar ices can be probed by studying the absorption bands they superimpose on the infrared radiation generated by stars in and behind interstellar clouds. A particularly instructive example of this is given in Fig. 9, which presents the infrared spectrum of W33A, a protostar embedded within a dust cloud that produces 50 to 100 magnitudes of foreground visual extinction (Willner, 1977; Capps *et al.*, 1978). One of the strongest features in the spectrum is the "10 μm " silicate feature discussed earlier. However, a number of other absorption features due to ices and related materials are also present. For those interested in modeling and quantitative analysis of ice features, the optical constants and intrinsic absorption strengths of a large number of astrophysically-relevant ices can be found in d'Hendecourt and Allamandola (1986), Hudgins *et al.* (1993, 1994), and references therein. Recent reviews on interstellar ices can be found in Sandford (1996) and Schutte (1996). A brief summary of the identification of each of the various ice components is provided in the following sections.

H_2O —Comparisons of astronomical and laboratory infrared spectra make it clear that H_2O is the dominant ice component in dense interstellar clouds. At present, H_2O features near 3280 cm^{-1} ($3.05\text{ }\mu\text{m}$, O-H stretch, often referred to as the "3 μm " band), 1670 cm^{-1} ($6.0\text{ }\mu\text{m}$, H-O-H bend), 735 cm^{-1} ($13.6\text{ }\mu\text{m}$, H_2O libration), and 250 and 140 cm^{-1} (40 and $70\text{ }\mu\text{m}$, lattice modes) have all been detected in dense molecular clouds and all fit reasonably well with laboratory H_2O ice spectra (see Fig. 9a,c; Soifer *et al.*, 1976a; Tielens *et al.*, 1984; Cox, 1989; Omont *et al.*, 1990). The 3280 cm^{-1} O-H stretching band of H_2O is typically one of the strongest in the interstellar spectra. Consequently, it was one of the first features to be detected and identified in dense clouds and there is extensive astronomical and laboratory literature dealing with this feature. Good discussions can be found in Hagen and Tielens (1981), Knacke *et al.* (1982), Leger *et al.* (1983), Smith *et al.* (1989, 1993), and Sato *et al.* (1990), just to name a few papers.

CH_3OH —The spectra of embedded protostars often contain a prominent absorption feature peaking near 1460 cm^{-1} ($6.85\text{ }\mu\text{m}$) (Puetter *et al.*, 1979; Tielens *et al.*, 1984; Tielens and Allamandola, 1987). While the profile of this feature varies substantially from

object to object, indicating the presence of more than one absorbing species, it was suggested early on that much of the absorption at this position might be due to the CH deformation mode vibration of methanol (Hagen *et al.*, 1980). This identification is supported by the laboratory spectra of CH₃OH-containing ices, which agree very well with the simpler astronomical band profiles (Fig. 9c).

However, this identification suggested that some clouds had ices with CH₃OH/H₂O ratios as high as 0.5. Such high abundances of methanol were hard to understand in terms of the gas-phase chemistry models of the time (although current gas-grain models may partially alleviate this problem). It was also suggested the 1460 cm⁻¹ feature might be partially or totally due to the asymmetric C-O stretch of carbonate minerals (Knacke and Krätschmer, 1980; Sandford and Walker, 1984, 1985; Hecht *et al.*, 1986). Thus, the unequivocal identification of methanol required the detection of its other bands, which were subsequently found. At present, additional methanol ice features that have been detected include ones at 4141 cm⁻¹ (2.415 μm, Sandford *et al.*, 1993), 2825 (Fig. 9b), 2600, and 2540 cm⁻¹ (3.54, 3.85, and 3.94 μm, Allamandola *et al.*, 1992), and 1125 and 1035 cm⁻¹ (8.9 and 9.65 μm, Skinner *et al.*, 1992).

The CH₃OH/H₂O ratios implied by the other identified bands are typically closer to 0.1, rather than the 0.5 implied by the 1460 cm⁻¹ band. Even at these lower concentration levels, CH₃OH, when present, is often the second most abundant component of the ice after H₂O. The lower CH₃OH/H₂O ratios suggest, however, that much of the absorption around 1460 cm⁻¹ is due to other species, which is consistent with the observed variability of the profile of this feature. The identities of these other species are presently unknown, although carbonates and aliphatic organic compounds are candidates (*cf.*, Allamandola and Sandford, 1988). As will be described later, the presence of CH₃OH has profound effects on the irradiation chemistry of these ices.

CO—After H₂O, the most studied interstellar ice component is probably CO. Carbon monoxide in the solid state produces a C≡O stretching absorption feature near 2140 cm⁻¹ (4.67 μm) whose spectral position, width, and profile are a sensitive function of the ice matrix within which the CO molecules are frozen (Sandford *et al.*, 1988). Although its identification is based on only one band, its unique position and excellent match with lab data allow its unequivocal assignment. Many, but not all, of the lines-of-sight that contain H₂O ice also contain CO ice and the relative strengths of the H₂O and CO bands indicate that CO/H₂O ratios range from 0.0 to 0.2 (Lacy *et al.*, 1984; Tielens *et al.*, 1991; Geballe, 1986; Eiroa and Hodapp, 1989; Whittet and Duley, 1991; Chiar *et al.*, 1995). Interestingly, the position and profile of the interstellar CO ice band varies from cloud to cloud (Fig. 11). A few of the CO bands have positions and profiles consistent with the majority of the CO being frozen in H₂O-rich matrices. However, the majority exhibit profiles indicative of CO frozen in nonpolar matrices (*i.e.*, in ices dominated by molecules like CO, CO₂, O₂, N₂, and CH₄, rather than H₂O; Sandford *et al.*, 1988; Tielens *et al.*, 1991). These are precisely the sorts of mantles predicted to be present in cloud regions where the H/H₂ ratio is <1 (Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985). The fact that H₂O, a highly polar molecule, is the most abundant molecule in the ices along all these lines-of-sight but that CO is generally in ices dominated by nonpolar molecules provides clear evidence for the existence of multiple chemical environments within individual cloud complexes. Thus, it would appear that interstellar clouds are not compositionally homogeneous, at least in their volatile contents.

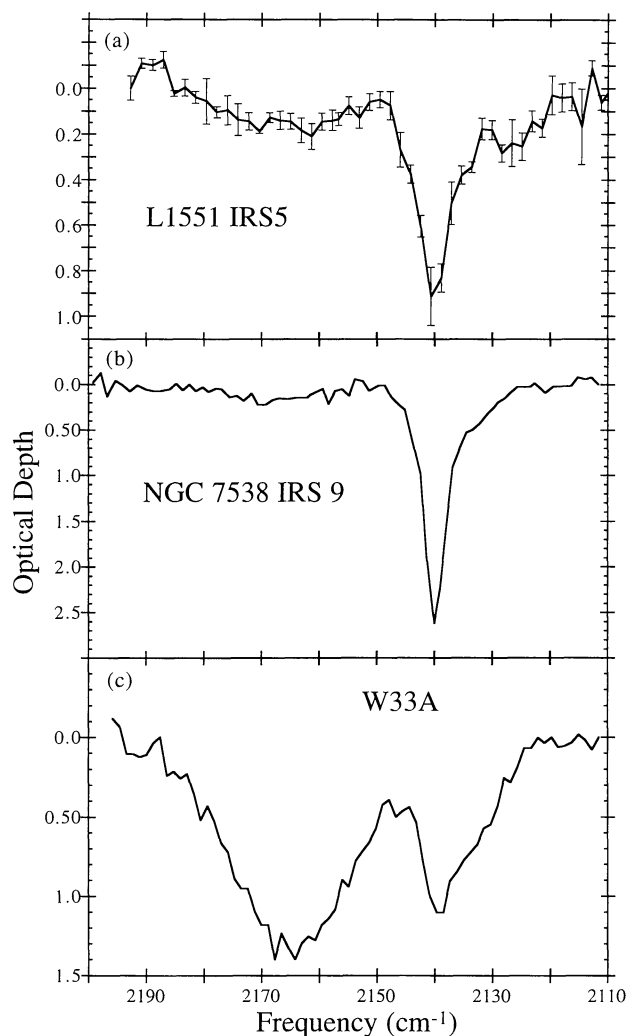


FIG. 11. The 2200–2110 cm⁻¹ (4.55–4.74 μm) spectra of several objects embedded in dense molecular clouds. The spectra show a wide range of relative strengths of the 2140 cm⁻¹ and 2165 cm⁻¹ absorption bands, demonstrating that they are due to different materials. The 2165 cm⁻¹ band is thought to be produced by a nitrile or (more likely) isonitrile. The feature near 2140 cm⁻¹ is due to CO frozen in ices. Most objects produce the narrow CO features seen in the top two spectra. These features are produced by CO frozen in nonpolar ices. Some objects (see the bottom spectrum), however, produce broader bands characteristic of CO frozen in polar, H₂O-rich ices. (Figure adapted from Tegler *et al.*, 1993.)

The "XCN" Feature—The spectra of a limited number of lines-of-sight through dense clouds contain a broad, often weak feature centered at ~2165 cm⁻¹ (4.62 μm) near the CO ice feature (Fig. 11; Lacy *et al.*, 1984; Tegler *et al.*, 1993; Weintraub *et al.*, 1994). While the statistics are currently poor, there is an indication that this feature is present only in the spectra of objects embedded within the clouds and not in the spectra of background stars (Tegler *et al.*, 1995). This suggests that the carrier of the feature may be associated with the local environment of the embedded star.

The molecule(s) responsible for this absorption have yet to be conclusively identified, although a number of suggestions have been put forward. Early laboratory experiments by Moore *et al.* (1983) and Lacy *et al.* (1984) demonstrated that a feature similar to the observed interstellar band was produced when laboratory ice mix-

tures were exposed to ion bombardment or ultraviolet radiation. Lacy *et al.* further noted that the feature was only produced by ices containing C and N and that good matches to the interstellar band position and width required that the ices be within specific temperature ranges. This, in conjunction with the feature's position, lead them to suggest that the absorption is due to the stretching vibration of a $C\equiv N$ functional group in a larger molecule (*i.e.*, a nitrile or isonitrile, usually designated as $X(CN)$, $X(C\equiv N)$, or XCN) and that some form of energetic processing is needed to produce it. Subsequent laboratory irradiation experiments on more astrophysically-relevant ice mixtures have shown that excellent spectral fits to the astronomical data can be obtained independent of ice temperature (Tegler *et al.*, 1993; Bernstein *et al.*, 1995).

Several alternate assignments for this band have also been suggested. It has been suggested the band might be due to the Si-H stretching vibration (Nuth and Moore, 1988; Moore *et al.*, 1991). However, the SiH feature seen in published laboratory spectra are too broad ($50\text{--}200\text{ cm}^{-1}$, as compared to $\sim 25\text{ cm}^{-1}$ for the interstellar feature) and the narrowest bands do not match in position (2270 cm^{-1} for SiH as opposed to 2165 cm^{-1} in the astronomical spectra). Thus, an explanation in terms of Si-H stretching presently seems unlikely. It has also been suggested that the band could be due to the CN stretch in the OCN^- ion (Grim and Greenberg, 1987). However, recent laboratory work done at NASA-Ames using isotopically-spiked starting materials casts doubts on this possibility (unpublished data).

H_2 —Laboratory studies of interstellar ice analogs have shown that ion and UV irradiation produces molecular hydrogen (H_2) within the ices (Moore and Hudson, 1992; Sandford and Allamandola, 1993b). This process can be quite efficient and the lab studies have demonstrated that it is possible that up to one-third of the molecules in interstellar ices could be H_2 ! In addition, despite the volatility of H_2 , the H_2O - H_2 binding energy is sufficiently high that a monolayer of H_2 can condense directly out of the gas phase onto H_2O -rich interstellar ices (Sandford and Allamandola, 1993b). If interstellar ices are porous, this could also lead to large abundances of H_2 on interstellar grains (Buch and Devlin, 1994; Dissly *et al.*, 1994). Still, it came as a surprise to many to find that interstellar ices do, at least along the line-of-sight to the object WL5 in the ρ Oph cloud, appear to contain H_2 as measured by the detection of its H-H stretching fundamental at 4141 cm^{-1} ($2.415\text{ }\mu\text{m}$, Fig. 12, Sandford *et al.*, 1993)! To date, this feature has not been seen (or searched for) in the spectra of any other objects. Given the potentially high abundance this molecule could have in interstellar ices and the importance it could play in their sublimation behavior, a more comprehensive search for this feature is clearly in order.

Other Species—Based on limited telescopic observations, laboratory studies of ice analogs, and theoretical chemistry models, a number of additional molecular species are suspected of being present in interstellar ices in quantities on the order of a few percent relative to H_2O . Species identified or tentatively identified in small numbers of objects include CH_4 (Lacy *et al.*, 1991), CO_2 (d'Hendecourt and Jourdain de Muizon, 1989), HCO and H_2CO (*cf.*, Tielens and Allamandola, 1987; Schutte *et al.*, 1994), OCS (Palumbo *et al.*, 1995), and possibly ketones and/or aldehydes (Tielens and Allamandola, 1987) and NH_3 (Hagen *et al.*, 1980; Knacke *et al.*, 1982). Many of these species, as well as a host of others, are predicted on the basis of interstellar chemistry models (*cf.*, Tielens and Hagen, 1982; d'Hendecourt *et al.*, 1985; Charnley *et al.*, 1995) and

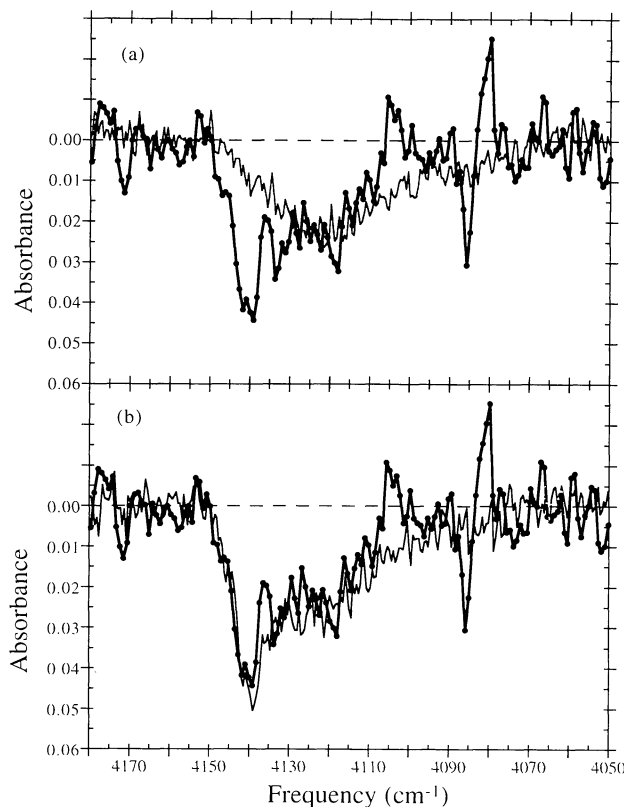


FIG. 12. A comparison between the optical depth spectra of WL5 (thick line with points) and two laboratory interstellar ice analogs (thin lines): (a) WL5 compared with an $H_2O:CH_3OH = 100:50$ ice deposited at 10 K, (b) WL5 compared with an $H_2O:CH_3OH:H_2 = 100:50:10$ ice deposited at 15 K. The narrower absorption near 4141 cm^{-1} ($2.415\text{ }\mu\text{m}$) is due to H_2 frozen in an H_2O -rich ice. The broader absorption feature near 4125 cm^{-1} ($2.424\text{ }\mu\text{m}$) is an overtone/combination band produced by CH_3OH in the ice. (Figure adapted from Sandford *et al.*, 1993.)

laboratory studies of the thermal and irradiation chemistry of ice analogs (*cf.*, Moore *et al.*, 1983; Agarwal *et al.*, 1985; Johnson *et al.*, 1986; Allamandola *et al.*, 1988; Bernstein *et al.*, 1995).

Of course, any species observed in the gas phase in dense clouds by radio or infrared techniques should also be in the grain mantles. At the low temperatures characteristic of these environments, all molecules should be strongly depleted by condensation onto the ice mantles (*cf.*, Sandford and Allamandola, 1993a). This includes species like polycyclic aromatic hydrocarbons (PAHs), which on the basis of infrared observations are thought to be abundant in the gas phase in more diffuse environments (*cf.*, Allamandola *et al.*, 1989a). In this regard, it is intriguing that a weak band has been detected near $3.25\text{ }\mu\text{m}$ in the spectra of several dense clouds (Brooke *et al.*, 1995; Sellgren *et al.*, 1995). This spectral position is characteristic of the aromatic C-H stretch. Clearly, a search for other aromatic bands in the spectra of dense clouds would be useful.

Photolysis Products in the Ices—As discussed earlier, the ices in dense molecular clouds are expected to be irradiated by UV photons and cosmic rays. This radiation will result in the breaking and rearrangement of chemical bonds within the ice, causing the destruction of some species and the creation of others. This is an important process since it can result in the creation of molecular species, particularly complex ones, that cannot be made via gas-

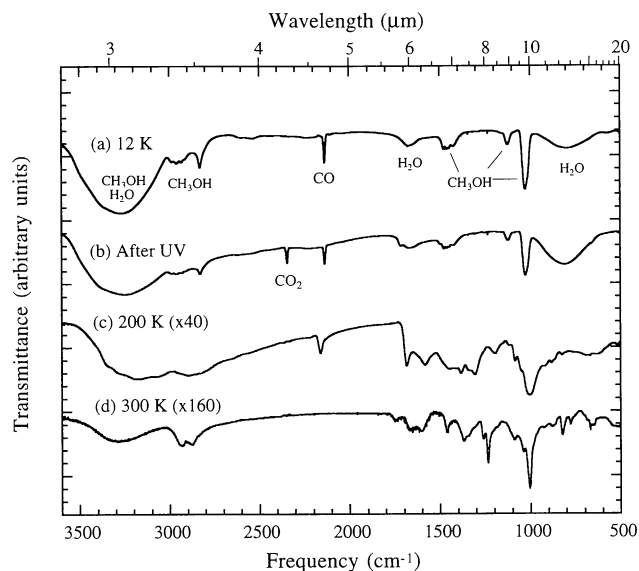


FIG. 13. The effects of UV photolysis on an interstellar ice analog. The 3600–500 cm^{-1} (2.78–20.0 μm) infrared spectra shown here are of: (a) a single layer $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3 = 100:50:10:10$ ice mixture deposited and maintained at 12 K prior to UV photolysis, (b) the same ice layer after UV photolysis at 12 K for ~ 20 h, (c) the residue remaining after 20 layers of the same ice mixture have been sequentially deposited and UV irradiated at 12 K and then the total sample is warmed to 200 K, and (d) the same sample shown in (c) after warming to 300 K. At temperatures > 150 K, all the surviving starting materials rapidly sublime away and the remaining material consists of a mixture of more refractory organic compounds (see text). (Figure adapted from Bernstein *et al.*, 1995.)

phase and gas-grain reactions at the low temperatures and pressures characteristic of dense clouds.

Figure 13 shows the evolution of the composition of an interstellar ice analog as it is subjected to irradiation by UV photons. The exposure to UV results in the destruction of several species (particularly CH_3OH) and the creation of others (HCO , H_2CO , CH_4 , CO_2 , HCN , *etc.*). Many of these new species have been identified, or tentatively identified, in interstellar ices. However, in most cases, their detection in interstellar spectra does not necessarily imply that radiation processing is responsible since many of these molecules would also be predicted by gas-phase or gas-grain chemistry models to be present (*cf.*, Tielens and Hagen, 1982). Presently the strongest evidence that radiation processing is important, at least in some locations within dense clouds, is provided by the "XCN" feature, which cannot be explained by any of the more abundant species predicted by gas and gas-grain chemical models but which is made by the photolysis of virtually any ice containing both C and N. For a more detailed description of the results of ice irradiation experiments, see Hagen *et al.* (1979), Agarwal *et al.* (1985), d'Hendecourt *et al.* (1986b), Allamandola *et al.* (1988), and Bernstein *et al.* (1995).

Organics in the Interstellar Medium

The same ice irradiation processes that produce the simpler molecules like CO , CO_2 , HCO , H_2CO , CH_4 , *etc.*, also result in the production of more complex species. Figure 13c and d show example spectra of the nonvolatile material that remains after an interstellar ice analog is irradiated and warmed. These laboratory simulations indicate that additional species like ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), amides (such as formamide, HC(=O)NH_2 , and acetamide, $\text{CH}_3\text{C(=O)NH}_2$),

nitriles and isonitriles ($\text{R-C}\equiv\text{N}$ and $\text{R-N}\equiv\text{C}$), ketones (R-C(=O)-R'), hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$), and compounds related to polyoxymethylene (POM, $(-\text{CH}_2\text{O}-)_n$) should all be present (Schutte *et al.*, 1993b; Bernstein *et al.*, 1995). Clear-cut evidence for these types of species in interstellar clouds is presently lacking, although some of the spectral structure detected in the 2000–1250 cm^{-1} region is consistent with the presence of such molecules. Since these materials are of exobiological interest, a rigorous search for absorption features due to these materials in dense clouds would clearly be of value.

In contrast to the dense ISM, there is excellent evidence for the presence of organics in the diffuse ISM. As early as 1976, absorption bands near 3300 and 2950 cm^{-1} (3.0 and 3.4 μm ; due to O-H and C-H stretching vibrations, respectively) were detected in the spectra of Galactic Center infrared sources (Soifer *et al.*, 1976b; Willner *et al.*, 1979; Wickramasinghe and Allen, 1980). This discovery led to many follow-up observations and analyses because the features along this line-of-sight were thought to be due to dust in the diffuse, rather than dense, ISM (Willner and Pipher, 1982; Jones *et al.*, 1983; Wickramasinghe and Allen, 1983; Butchart *et al.*, 1986). However, these studies of the Galactic Center did not confirm that the dust responsible for the features was in the diffuse medium, since the features could have been produced by materials local to the Galactic Center itself. Indeed, McFadzean *et al.* (1989) showed that the O-H feature varies in strength from source to source in the Galactic Center, suggesting that it is due in large part to local materials. Additional studies along different lines-of-sight were needed to ascertain how much of the 3300 and 2950 cm^{-1} (3.0 and 3.4 μm) absorption bands arises from the intervening ISM.

Recent studies of the 3600–2600 cm^{-1} (2.78–3.85 μm) spectral region of objects along many different lines-of-sight suffering from a wide range of visual extinctions (A_V) have clarified this issue considerably (Sandford *et al.*, 1991, 1995; Pendleton *et al.*, 1994). These studies demonstrated that the 3300 cm^{-1} (3.0 μm) O-H stretching band does not correlate with A_V along different lines-of-sight and therefore is not due primarily to dust in the diffuse ISM, confirming the conclusions of McFadzean *et al.* (1989). In contrast, the 2950 cm^{-1} (3.4 μm) C-H stretching band shows a remarkable similarity in position and profile over extinctions ranging from as low as 3.9 to as high as 31 (see Fig. 14a). In addition, the strength of this feature increases with increasing A_V as would be expected for dust in the diffuse ISM (see Fig. 7).

The profile and subpeak positions of the overall C-H stretching feature provide specific clues to the nature of the carbonaceous material in the diffuse ISM. The feature extends from ~ 3000 to 2800 cm^{-1} (3.33–3.57 μm) with subfeatures near 2955, 2925, and 2870 cm^{-1} (3.38, 3.42, and 3.48 μm) (Fig. 14a). The positions of the first two of these subfeatures are characteristic of the asymmetric C-H stretching frequencies of $-\text{CH}_3$ (methyl) and $-\text{CH}_2-$ (methylene) groups in saturated aliphatic hydrocarbons (molecules with the formula C_nH_{n+2}). The relative strengths of these two subfeatures indicate that the average $-\text{CH}_2-/-\text{CH}_3$ ratio of the interstellar hydrocarbon is 2.5 ± 0.4 . The absolute strengths of these bands indicates that this material accounts for at least 2.5% of the total cosmic C in the diffuse ISM, and probably closer to 10%. However, the interstellar band profile differs from that of pure saturated aliphatic hydrocarbons in that it does not contain the two peaks near 2870 and 2850 cm^{-1} (3.48 and 3.51 μm) characteristic of the symmetric C-H stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively but instead shows only a single subfeature near 2870 cm^{-1} .

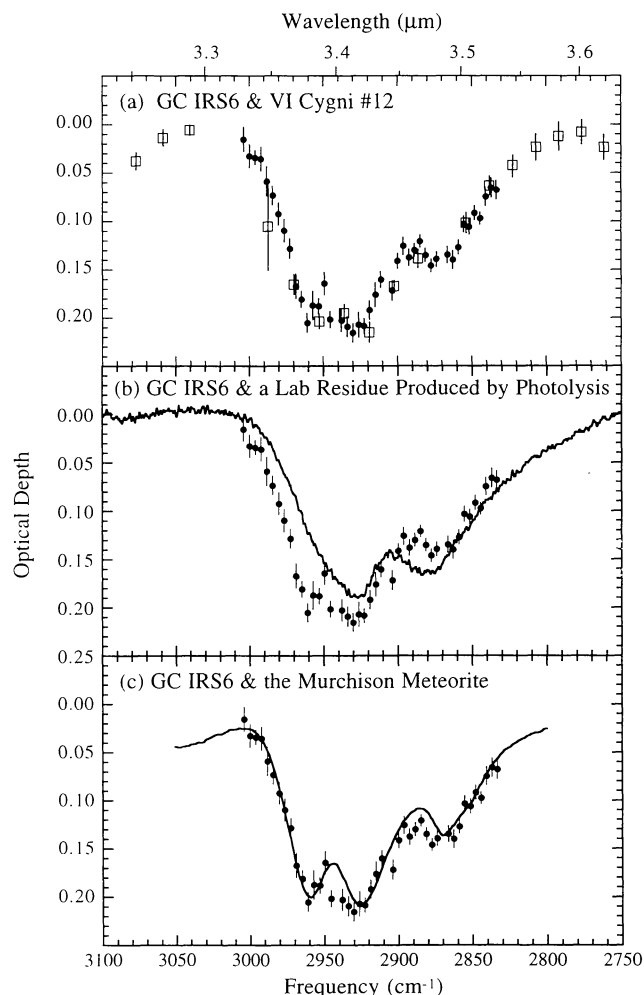


FIG. 14. A comparison of the optical depth profile of the C-H stretching band due to dust in the diffuse ISM towards GC IRS 6E ($A_V = 31$ mag; filled circles) and: (a) VI Cyg #12 ($A_V = 10$ mag; open squares). The VI Cyg #12 data has been scaled to have the same optical depth as the GC IRS 6E data at 2925 cm^{-1} . (b) A C-rich laboratory residue produced by the irradiation of an interstellar ice analog (solid line) (see Bernstein *et al.*, 1995 for details on the production of the laboratory residue). (c) A carbonaceous phase of the Murchison meteorite (solid line) (see Pendleton *et al.*, 1994). A comparison of the diffuse ISM C-H stretching feature to the dense medium feature identified with interstellar microdiamonds can be found in Fig. 10. (Figure adapted from Sandford *et al.*, 1995.)

($3.48\text{ }\mu\text{m}$). Electronegative or other perturbing chemical groups at the end of short chain aliphatics can suppress the 2850 cm^{-1} ($3.51\text{ }\mu\text{m}$) feature without greatly effecting the positions or strengths of the other C-H bands. Thus, laboratory data suggests that the 2950 cm^{-1} ($3.4\text{ }\mu\text{m}$) C-H stretch feature due to dust in the diffuse ISM is largely produced by short ($n = 2-4$) aliphatic chains like $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ attached to electronegative or other perturbing chemical groups like $-\text{O}-\text{H}$, $-\text{C}\equiv\text{N}$, aromatics, *etc.*, (see Sandford *et al.*, 1991 for a more detailed discussion on the spectral constraints on the diffuse C-H carrier).

Additional constraints on the nature of this material can be provided by spectral comparison with laboratory materials. Pendleton *et al.* (1994) compared the interstellar feature with the spectra of various carbonaceous materials suggested to be in the ISM. These include the residues formed by the warming of UV photolyzed

interstellar ice analogs mentioned above (Fig. 14b), amorphous carbons like Hydrogenated Amorphous Carbon (HAC; *cf.*, Duley, 1994) and Quenched Carbonaceous Composite (QCC; Sakata and Wada, 1989), and a carbonaceous fraction of the primitive meteorite Murchison (Fig. 14c). All these materials provided qualitative fits to the interstellar feature, but the match provided by the meteoritic material was clearly best. This suggests that the perturbing chemical groups inferred from the profile of the interstellar feature may largely consist of aromatic moieties since meteoritic kerogen is rich in aromatics. In this regard, the tentative detection by Pendleton *et al.* (1994) of a weak absorption feature near 3030 cm^{-1} ($3.3\text{ }\mu\text{m}$) in the spectra of several Galactic Center objects may be especially important. This spectral position is characteristic of the aromatic C-H stretching vibration and suggests that aromatic materials may be present in the diffuse dust in significant concentrations. Given their known presence in the gas phase, it would not be surprising to find PAHs in interstellar solids.

As an aside, it is interesting to note that the strength of the C-H stretching feature scales linearly with visual extinction along all the lines-of-sight so far examined except for objects near the center of the Galaxy (Sandford *et al.*, 1995). This behavior parallels that seen by Roche and Aitken (1985) for the Si-O stretching band due to silicates in the diffuse ISM (see Fig. 7). The deviation of Galactic Center objects from the linear trend implies that the grains responsible for the diffuse ISM aliphatic C-H and silicate Si-O stretching bands are different from those responsible for much of the observed visual extinction. The similar behavior of the C-H and Si-O stretching bands also suggests that these two components may be coupled, perhaps in the form of silicate-core, organic-mantle grains, and that they may not be uniformly distributed within the galaxy. Sandford *et al.* (1995) present several possible models of the distribution of this material and show that the inner parts of the Galaxy may have band carrier densities that are 5 to $35\times$ higher than in the local ISM.

It is not clear what bearing these organics have on the inventory of materials present during the formation of new planetary systems in dense molecular clouds. Since interstellar materials are thought to cycle between the dense and diffuse interstellar media, one would expect that the organics seen in the diffuse ISM might be present in the dense ISM as well. However, the diffuse ISM C-H stretching absorption features are not seen in the spectra of dense clouds, even though abundance arguments suggest that they should be easily detectable (Allamandola *et al.*, 1992, 1993). The reason for this is not currently understood and at face value seems to challenge the paradigm that the diffuse and dense media mix efficiently. Perhaps the organic materials in the diffuse ISM are selectively modified or destroyed during incorporation into dense clouds. Perhaps the C-H stretching feature is masked in some way by the presence of ices (in most dense clouds the " $3.0\text{ }\mu\text{m}$ " H_2O ice features show an unexplained broad, featureless long wavelength wing that covers the C-H stretching region; *cf.*, Smith *et al.*, 1993). In any event, there is presently no unequivocal evidence that the organics seen in the diffuse ISM survive incorporation into dense clouds!

SOME ASTROPHYSICAL IMPLICATIONS AND PROBLEMS

It is clear from the previous discussion and citations that the study of interstellar dust has enjoyed a renaissance in recent years. We have learned more about the composition of interstellar dust in the past decade than was discovered in all years previous. However, as Table 1 summarizes, it is now apparent that the population of

materials in the ISM is far more complex and diverse than anyone would have imagined 20 years ago. The result is a "target-rich" environment for future studies. In the following sections, I will try to briefly summarize several areas in which I feel important progress might be made in the near future. I will also offer several speculations and musings in the hope that they may inspire additional studies.

Interstellar Silicates in Meteorites and Interplanetary Dust Particles

While a variety of interstellar grains have now been found in meteorites, interstellar silicates have yet to be positively identified in these objects. Since there is a great deal of observational evidence that silicates are ubiquitous in the ISM and traces of more volatile materials have survived incorporation in the solar system (for example, the carriers of D-enrichments), some interstellar silicates should have survived as well. Why haven't they been found?

The current nondetection of interstellar silicates in meteorites may be the result of a collection of natural and technical constraints. First of all, it is possible that interstellar silicates do not carry significant isotopic anomalies. If this is the case, an analog of the step-wise acid dissolution techniques that have proven so useful for identifying interstellar diamonds, SiC, and graphite will not work since there will be no "tracer" to follow in the enrichment process. Furthermore, the "background" of solar materials is obviously much worse for silicates than for the SiC, *etc.*

Given the likelihood that meteorites and IDPs should contain some relatively unaltered interstellar silicates, meteoriticists need to ask themselves how they might be identified. Unfortunately, I have little advice to give with regard to how this might be done. Since silicates are removed in the very earliest stages of normal acid dissolutions, I suspect that they will most likely have to be searched for *in situ*. If interstellar silicates do not carry significantly anomalous isotopic signatures, it is not clear what signature should be searched for. Given that the spectral signatures of interstellar silicates suggest that amorphous materials dominate and that grain evolution models suggest that ~80% of the dust in the ISM has likely been destroyed and recondensed, perhaps searches should concentrate on finding amorphous or "glassy" silicates.

In this regard, the components referred to as Glass with Embedded Metal and Sulfides (GEMS) found in IDPs may be of particular interest. It is now well established that the population of microscopic interplanetary dust particles (IDPs) collected in the stratosphere contains a variety of grain types which probably come from both asteroids and comets (Flynn, 1989; Sandford and Bradley, 1989; Nier and Schlutter, 1992). (For more detailed reviews of the properties of collected IDPs, the reader is referred to Mackinnon and Rietmeijer, 1987; Sandford, 1987; Bradley *et al.*, 1988; and Brownlee and Sandford, 1992.) Since comets are generally considered to be relatively unprocessed objects, cometary dust might be expected to contain even larger contributions of relatively pristine interstellar grains than do meteorites. The IDPs that are thought to come from comets consist of assemblages of minerals, metals, and carbonaceous phases that are highly unequilibrated with respect to each other (*cf.*, Bradley and Brownlee, 1986; Bradley, 1994a,b).

A substantial fraction of the most likely cometary grains consists of smaller subgrains now referred to as GEMS (*cf.*, Bradley, 1988, 1994a,b). Most GEMS are between 0.05 and 0.5 μm in diameter, are somewhat aspherical, and have bulk compositions within a factor of three of solar for most major elements, although they do

generally have stoichiometric excesses of O. They largely consist of small grains of FeNi metal and FeNi sulfide crystals embedded in an amorphous or "glassy" silicate material. Compositional gradients within individual GEMS and the observed O excesses suggest that they have been exposed to large amounts of ionizing radiation prior to incorporation into their parent IDP (Bradley, 1994b). The composition, size range, morphology, and radiation exposure of GEMS are all consistent with many of the attributes expected of interstellar dust and suggest the possibility that GEMS may in fact be samples of interstellar dust. The small metal inclusions in GEMS fall in a size range ($<0.01 \mu\text{m}$) in which they would be expected to exhibit superparamagnetism. Thus, GEMS or related materials in the ISM would be expected to exhibit almost "perfect" alignment with respect to local magnetic fields. Therefore, GEMS have potentially important implications for issues associated with interstellar polarization (Martin, 1995).

If GEMS actually are relatively unaltered interstellar grains, then a more detailed knowledge of their composition and morphology is clearly important and the issues raised in Martin (1995) need to be addressed. For example, the abundance of atomic S in the ISM is apparently consistent with no S depletion into grains, but GEMS typically contain S at the few percent level (by atom number), which is a factor of 2 below solar but still requires the existence of some interstellar depletion. It is not presently clear whether this represents a problem or not. Further work on both interstellar depletions and GEMS should help address such issues. In any event, while the interstellar nature of GEMS has yet to be proven, they are definitely extraterrestrial, and I suspect that meteoriticists, theorists, and observers alike would benefit from further studies of these materials and careful consideration of their possible implications.

Further Spectropolarimetry

The identification of silicates from detection of the "10 μm " and "20 μm " silicate features in the ISM represents a case where long term repetition of an idea has come to substitute for true understanding. While there is little doubt that these features are associated with Si-O stretching and Si-O-Si bending mode vibrations in some sort of silicate-like material(s), astronomers should not feel content that they have "identified" the carrier of these bands. At present, next to nothing is known about the compositional and structural nature of this material. To say that we have identified the carrier of the interstellar 10 μm feature is comparable to a detective claiming to have solved the case because it is now known that the murderer is right-handed!

A much more comprehensive attempt needs to be made to detect and use spectral substructure within the silicate bands to identify specific mineral types and to better understand the degree of crystallinity (or lack thereof) of these materials. Even if crystalline minerals are rare in ISM, they may well prove to be the best way to constrain silicate elemental composition and will place significant constraints on the conditions to which the grains have been exposed. The detection of any variations in substructure as a function of environment could also be illuminating. For example, if silicates are continually destroyed, mixed, and reaccreted in the general ISM, then we might expect there to be measurable differences between the spectral features produced by interstellar and circumstellar dust (both dust being ejected from late-type stars and dust evolving in protostellar environments).

Significant progress in this area might best be made by carrying out more spectropolarimetry studies of the type done by Aitken *et*

TABLE 1: List of cosmic materials discussed in the text*

Component	Abundance	References
Circumstellar		
Silicates	—	Treffers and Cohen (1974), Merrill and Stein (1976), Knacke <i>et al.</i> (1993)
Amorphous Carbon [†]	—	Martin and Rogers (1987)
SiC	—	Treffers and Cohen (1974), Merrill and Stein (1976), Little-Marenin (1986), Baron <i>et al.</i> (1987)
Oxides	—	Cheeseman <i>et al.</i> (1989), Little-Marenin and Little (1990), Goebel <i>et al.</i> (1989), Sloan <i>et al.</i> (1996)
Diffuse ISM		
Silicates	>95% of Si and 20% of O	Roche and Aitken (1985), Tielens and Allamandola (1987)
SiC	<5% of Si	Whittet <i>et al.</i> (1990)
Graphite [‡]	~15% of C [‡]	Mathis <i>et al.</i> (1977), Draine (1989), Draine and Malhotra (1993)
Solid organics in aliphatic -CH ₃ and -CH ₂ - groups	>2.5% of C	Sandford <i>et al.</i> (1991, 1995), Pendleton <i>et al.</i> (1994)
Solid organics in aromatic structures	>5% of C	Pendleton <i>et al.</i> (1994)
Gas Phase PAHs	2–10% of C [§]	Allamandola <i>et al.</i> (1989a), Puget and Leger (1989)
Dense ISM		
Gas Phase Molecules (examples)	Typical Abundance Relative to H ₂	Mann and Williams (1980), Irvine and Hjalmarsen (1984), van Dishoeck <i>et al.</i> (1993)
H ₂	1	CO carries the majority of the C and O inventory in the gas phase (~10–20% of C and ~5–10% of O)
CO	10 ⁻⁴	
H ₂ O	10 ⁻⁵	
CH ₃ OH	10 ⁻⁶ or less	
NH ₃	10 ⁻⁷	
Most Other Molecules (~100 total)	10 ⁻⁸ to 10 ⁻¹²	
Mixed Molecular Ices	Typical Abundance Relative to H ₂ O	Tielens and Allamandola (1987), Sandford (1993), Schutte (1996)
H ₂ O	1	Total contribution of ice phase species can be as high as 40% of C and O
CO	0.1–0.4	
CH ₃ OH	0.1 or less	
H ₂	>0.01	
CH ₄	~0.02	
XCN	~0.02	
NH ₃	<0.1	
CO ₂	<0.1	
H ₂ CO	<0.1	
HCO	<0.1	
OCS	4 × 10 ⁻⁴	
Silicates	>95% of Si and 20% of O	Willner <i>et al.</i> (1982), Roche and Aitken (1984), Tielens and Allamandola (1987), Whittet <i>et al.</i> (1988)
Microdiamonds [#]	10–20% of C [#]	Allamandola <i>et al.</i> (1992, 1993), Brooke <i>et al.</i> (1995), Sellgren <i>et al.</i> (1995)
Solid organics in aromatic structures	~10% of C [§]	Brooke <i>et al.</i> (1995), Sellgren <i>et al.</i> (1995)

*The abundances listed in this table do not account for the possibility that some atoms are redundantly identified. For example, as discussed in the text, the microdiamonds and graphite could be the same material. See also Snow and Witt (1995) for a recent reevaluation of the cosmic abundance of C.

[†]Identification based on model fits to thermal excesses.

[‡]Graphite has not yet been detected in the ISM; abundances are based on theoretical considerations of how much graphite would be required to explain the 2175 Å feature.

[§]The abundance is based on the observed infrared fluorescence features seen in reflection nebulae, planetary nebulae, and photodissociation regions, all environments rich in UV radiation. It is thought that PAHs are widespread in the galaxy but they are only easily detectable in environments that favor the fluorescence process. Thus, the listed abundances for PAHs should be a lower limit. The C in PAHs is distributed fairly evenly between small PAHs (~25 C atoms) and larger PAHs.

[#]While microdiamonds have not been identified in the diffuse ISM because of spectral confusion with the spectral features due to aliphatic C-H stretching bands, current data are not inconsistent with microdiamonds accounting for comparable fractions of the cosmic C in both the dense and diffuse interstellar media (see Allamandola *et al.*, 1993).

[§]Estimate based on a rough analysis by the author on the data presented in Sellgren *et al.* (1995).

al. (1988). Such studies should provide additional information on the abundance of crystalline material and give clues as to its mineralogical identity. For example, one could address whether the source of the 11.3 μm "elbow" seen so commonly in the 10 μm feature is due to crystalline olivines, PAHs, or something else.

To a large extent, the same arguments apply to the SiC emission feature seen in circumstellar environments. While it is likely that this feature really is due to Si-C stretching mode vibrations, the compositional and structural nature of the carrier is essentially unknown and astronomers should not feel that this feature is truly "identified." Given the enormous wealth of data obtained from meteoritic samples of interstellar SiC in recent years, astronomers should revisit this issue. One obvious study to attempt is to apply the same spectrophotometric techniques that have yielded results in the 10 μm silicate feature to environments that show the SiC feature.

The Production of Organics in the Interstellar Medium

It is clear that organic materials are abundant in the ISM and that they are produced by a variety of processes. Thus, the organics in meteorites need not necessarily be the sole result of solar and parent body processes (as the measured D-enrichments attest), and the possibility that some of these materials may have an interstellar heritage needs to be continually kept in mind. The interstellar processes that produce organics include ion-molecule, gas-grain, and solid-state reactions resulting from both thermal processes and energetic processing by high-energy photons and cosmic rays. These different processes yield different products, different abundances, and, in some cases, different isotopic signatures. Searches for these signatures in meteoritic organics should prove to be extremely instructive.

For example, it is now clear that CH_3OH is often the second or third most abundant component in interstellar and cometary ices. The high abundance of CH_3OH is a key issue since its presence drives a rich interstellar photochemistry that efficiently produces a variety of organics, including hexamethylenetetramine (Bernstein *et al.*, 1995), a compound that decomposes in acidic solutions to form amino acids. The presence of CH_3OH also has profound effects on the physical behavior of ices (Blake *et al.*, 1991) and, since CH_3OH is often the second most abundant icy component in comets (*cf.* Reuter, 1992), this may have important implications for their vaporization behavior (Sandford and Allamandola, 1993a).

As an aside, the fact that CH_3OH appears to be more abundant than CH_4 in both interstellar and cometary ices suggests that this may also have been true of the material from which the solar nebula formed. Many models of the solar nebula assume that CH_4 is present but ignore CH_3OH (and its chemical products). Given the different physical and chemical properties of these two compounds, it is conceivable that this could make a significant difference in model predictions associated with redox issues, gas-solid interactions, and the like. Models using more realistic ice and gas compositions should be explored.

Deuterium Enrichments

The assumption that gas-phase ion-molecule reactions are responsible for the D-enrichments seen in the ISM and in meteorites has become something of a mantra to meteoriticists and astronomers alike. However, this is largely by virtue of this explanation having been accepted the longest to the exclusion of other possibilities. As discussed earlier, D-enrichments are expected to be produced in the ISM not only by ion-molecule reactions in the gas phase, but also by energetic processing of ice mantles, gas-grain reactions on ice

mantles, and unimolecular photodissociation reactions in large molecules like PAHs. All four of these mechanisms should be occurring in the ISM, but the latter ones are likely to be more important in the sense that they effect a larger fraction of the reservoir of interstellar material.

Given that the D-enrichments seen in meteorites may be the result of multiple processes, it behooves us to consider how we might detect and separate their individual products. Since the different enrichment processes are expected to affect different types of molecules differently, it would certainly be helpful to have a better understanding of the abundance and variety of molecular carriers of D. In this regard, continuing studies along the lines of Kerridge *et al.* (1987) would clearly be useful. As an example, the possibility that interstellar PAHs become D-enriched by unimolecular photodissociation reactions can be explored by studying the size dependence of the D-enrichment in aromatics in meteorites.

Where Are the Core-Mantle Grains?

At present, the information gleaned from interstellar materials in meteorites and IDPs has provided little evidence for core-mantle grain morphologies. This is an item of some concern since many interstellar grain models appeal to such structures; the correlation of interstellar silicates and organics in the diffuse ISM is consistent with core-mantle grains, and mantles should form in dense clouds. This would appear to be a serious issue and we need to consider how this apparent mismatch might be addressed.

Getting Data from Meteorites and Interplanetary Dust Particles into Interstellar Grain Models

The discovery of interstellar grains in meteorites represents a major advance in our understanding of interstellar dust and provides major constraints for interstellar grain modelers. As additional information is garnered from meteoritic samples, modelers will have to deal with more and more complex (and realistic) structures, compositions, *etc.*, in order to remain true to constraints provided by the collected dust (and, of course, new observations). However, I would expect the rewards of such activities to more than compensate for the required effort.

The modeling of grain destruction and evolution is one area where information from real interstellar grains should help considerably. The mere knowledge that interstellar grains have survived incorporation into meteorites has already constrained the range of viable dust evolution models. However, the measured abundances of different grain types, their grain size distributions, *etc.*, should increasingly allow modelers to hone our understanding of grain destruction processes. A key question to address is the rate at which grains are destroyed and then recondensed in the ISM (Jones *et al.*, 1994), as this may relate directly to the lack of any obvious isotopic anomalies associated with silicates.

Meteoritic data also needs to be fully incorporated into interstellar polarization and extinction models. Past models have often assumed idealized grains that lack the compositional and structural complexity of real materials. This was done in part because such simplifications make the computations considerably easier and in part because nobody knew what kinds of details were appropriate to add. However, with the advent of the meteoritic database, it should now be possible to begin to add "real-world" details, details that may ultimately prove to be critical. For example, if grain alignment in the ISM is the result of superparamagnetic processes, the presence of heterogeneity in GEMS in the form of small metal

inclusions may ultimately provide modelers with the information needed to quantify this process.

Are Meteoritic/Interstellar Diamonds Interstellar Graphite?

As discussed earlier, the interstellar graphite grains found in meteorites are not the same graphite particles inferred to be responsible for the interstellar 2175 Å extinction feature, nor are these two types of grains size end-members of the same grain population. An explanation of the interstellar 2175 Å feature in terms of graphite requires extremely small grains (radii ≤ 150 Å), while the meteoritic grains are enormously larger (typical radii of 1 to 5 μm).

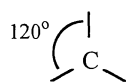
At this point, it is worth digressing to review how small graphite grains are thought to produce the 2175 Å extinction feature (see Draine, 1989 for a more thorough discussion). Using the bulk dielectric constants of graphite, it can be shown that small spheres satisfy the conditions needed to sustain "surface plasmons" at $\lambda = 2700$ and 2200 Å. At small grain sizes (radii < 50 Å), the result is a 2200 Å feature due almost entirely to absorption. For grains with radii > 100 Å, scattering also becomes significant at 2200 Å. Graphite's special ability to generate such plasmons is the result of its aromaticity; delocalized π electrons in the structure are free to wander the surface of the grain and it is these electrons that "carry" the plasmon. For particles with radii < 100 Å, the position of the feature is largely independent of particle size, but as the grain size increases, the feature shifts to lower frequencies (physicists will recognize this as a sophisticated variant on the particle in a box problem). Under these assumptions, $\sim 15\%$ of cosmic C would need to be in the radius ≤ 150 Å range to explain the strength and position of the observed interstellar 2175 Å feature.

However, several considerations complicate this simple picture. First, it is not clear whether the bulk dielectric constants of graphite are appropriate for 100 Å grains. Indeed, the limited experimental evidence in the ultraviolet obtained from arc-produced graphite particles suggests it is possible they are not (Day and Huffman, 1973). Additionally, the absorption is expected to be modified to varying degrees if one assumes nonspherical particles, grain size distributions, grain coatings, varying temperatures, *etc.*, (again, see Draine, 1989 for a review). Despite these complications, several major themes persist in all the graphite-based models: (1) the grains must be small if the resulting absorption feature is to match the position of the interstellar feature, (2) a significant fraction (on the order of 15%) of the cosmic C needs to be in these small grains to explain the strength of the interstellar feature, and (3) the grains need to be graphitic in the sense that they must have surfaces with delocalized electrons so surface plasmons can exist.

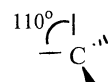
The interstellar graphite grains found in meteorites fail the first two of these criteria. However, I submit that the *microdiamonds* found in meteorites and detected in the ISM might meet all three requirements. First, the observed meteoritic diamonds fall in a size range measured in tens of angstroms rather than microns and are therefore much closer to the inferred interstellar graphite sizes than are the meteoritic graphite grains. Second, both astronomical and meteoritic evidence suggests that microdiamonds may exist in appropriate abundances. The highest diamond abundances typically found in meteorites are on the order of a few percent of the C (*cf.*, Huss and Lewis, 1995). This suggests that the abundance of this material in the ISM is at least this high since some of the interstellar diamond population was presumably destroyed during incorporation into the solar nebula and during subsequent parent body alteration processes. Additionally, the optical depth of the interstellar 2880

cm^{-1} band identified with microdiamonds indicates that a *minimum* of $\sim 5\%$ of the available cosmic C is tied up in this material (Allamandola *et al.*, 1992). Thus, the amount of cosmic C tied up in microdiamonds appears to be on the order of the required abundances needed to explain the 2175 Å feature using graphite.

This leaves only the criterion that the microdiamonds need to "behave like graphite" in the sense of having surfaces with delocalized electrons that produce surface plasmons. Again, there is evidence to support this possibility. Electron microscope studies of the meteoritic diamonds have shown that these materials contain substantial sp^2 (aromatic or "graphitic") bonding in addition to the expected sp^3 (aliphatic or "diamond") bonding (Blake *et al.*, 1988; Bernatowicz *et al.*, 1990). A diagram showing the difference between sp^2 and sp^3 bonding is given below.



sp^2 (planar or graphitic)



sp^3 (tetrahedral or diamond-like)

The presence of sp^2 bonding requires π -type bonding in "graphitic or amorphous" regions, probably the grain surfaces. Thus, the meteoritic interstellar diamonds may have some of the aromatic qualities required by the models used to explain the interstellar 2175 Å feature.

The presence of aromatic domains on microdiamonds is not entirely unexpected. Carbon atoms at the surface of a diamond have an unsatisfied bond. This bond can be accommodated by a terminating atom (typically an H atom in macroscopic diamonds) or by the formation of a double bond with an adjacent atom having the same problem. In the former case, the C maintains an sp^3 diamond-like bonding, while in the latter, an sp^2 aromatic bonding results. The surfaces of microdiamonds in the ISM may well be even more aromatic than those found in meteorites. The meteoritic microdiamonds have been wrested from the meteorites by multiple exposures to acids. Thus, many of the preexisting surface sp^2 bonds may have had an opportunity to accept a proton and convert to a terminal sp^3 C-H bond.

The possibility that the meteoritic/interstellar microdiamonds do double duty as interstellar graphite could have implications for at least one additional issue. A recent reappraisal of the interstellar C budget suggests that the ISM may contain substantially less total C than previously thought (Snow and Witt, 1995). If this is the case, many interstellar dust models, especially those that appeal to large amounts of hydrogenated amorphous carbon (HAC) and graphite, are in serious danger of oversubscribing the available C. This problem may be partly alleviated, at least for models that appeal to graphite, if it turns out that the microdiamonds and the graphite are actually the same component.

Thus, I would submit that the interstellar diamonds found in meteorites and identified in the ISM may be the same material that modelers of the 2175 Å feature call graphite! Of course, the proceeding discussion is obviously quite speculative. However, the possibility has many attractive features and I think it is worth pursuing. This could conceivably be done in a number of ways. Determination of the optical properties of the meteoritic diamonds could be of immense use, although changes produced in their surfaces by the acid-dissolution process may complicate the issue. In addition, modelers should consider whether only graphite can match the inter-

stellar 2175 Å feature or whether this might be done with particles consisting of microdiamond "cores" having partially or largely aromatic surfaces. Perhaps the variations seen in the position and profile of the 2175 Å band are due to differences in the degree and connectivity of aromatic surface coverage?

CONCLUSIONS AND A LOOK TO THE FUTURE

Tremendous progress has been made in the field of interstellar dust in recent years through the use of telescopic observations, theoretical studies, laboratory studies of analogs, and the study of actual interstellar samples. We now know that the interstellar medium contains an enormous diversity of materials created by a wide range of chemical and physical processes and it is clear that we have only begun to understand this complexity. This is a far cry from the picture of interstellar materials that would have been presented just two decades ago, a picture in which only a few generic types of grains might have been mentioned and the possibility of the presence of molecules barely discussed!

In this paper I have reviewed what we know about the more abundant materials we think exist in the ISM. I have also discussed some of the implications resulting from this knowledge and considered a number of areas in which future work might be expected to yield important results. Despite the length of this paper, much has been left unsaid, both about what we know and what we don't. Nonetheless, it is clear that, given the recent rapid expansion of our knowledge in this field, one of the main things we should be doing in the future is exactly the sorts of things we have been doing! The combined efforts of observational and laboratory studies should continue to yield exciting results leading to an improved understanding of the dust components we already know about and the identification of entirely new components. Increased contact between the astronomy and meteoritics communities can only accelerate this process.

As a final look to the future, I would draw the reader's attention to an important future source of information on interstellar dust, namely the STARDUST Mission. STARDUST was recently selected by NASA to be the next Discovery mission. The mission involves launching a spacecraft in 1999 that would subsequently make a low velocity (~5.4 km/s) flyby of the periodic comet Wild-2 in 2003, where it would sweep up dust from the coma using aerogel collectors. While on route to and from the comet, it will also collect contemporary interstellar dust grains during certain portions of its three orbits of the Sun. Both the cometary and interstellar samples will be returned to Earth in 2006 where they will be made available to the general scientific community for study. The future clearly holds a lot of excitement for those of us interested in interstellar materials!

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